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Fungal metabolite screening: database of 474 mycotoxins and fungal metabolites for dereplication by standardised liquid chromatography–UV–mass spectrometry methodology

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Abstract

A standardised LC–UV–MS micro-scale method for screening of fungal metabolites and mycotoxins in culture extracts is presented. The paper includes data for detection and dereplication of >400 fungal metabolites to facilitate detection and identification when standards are not available. The data also shows the types of components that can be analysed by positive electrospray (ESI^+) mass spectrometry (MS) along with common fragments and adducts of these, as well as giving suggestions on whether UV or ESI^+-MS methods should be used. Examples of dereplication of penitrems and macro-cyclic trichothecenes, and detection of several novel compounds are shown. This was done by UV spectroscopy combined with accurate mass determination of adduct and fragment ions obtained by high-resolution orthogonal time-of-flight MS.
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1. Introduction

Microfungi are a rich source of chemical diversity [1–3], and together with the actinomycetes they are the source of more than 50% of metabolites utilised by the pharmaceutical industry in either the native form or as derivatives [4–7]. As only a small part of the mycota is known and most fungi produce several unknown metabolites, fungi are still one of the most promising microbiotic sources for new lead compounds. Hence fungi are the objective in numerous high-throughput screening (HTS) programs targeting new pharmaceutics and other bioactive components [8–10]. Since isolation and characterisation of ''new'' candidates are very time consuming and costly [9] it is important to develop an early and quick dereplication approach to eliminate already known components and to avoid mycotoxin producing species [11].

To optimise the output of HTS screening programs, it is of utmost importance to use all á priori knowledge about the organisms, thus species, subgenus or genus will provide information of their bio- and chemodiversity, ecology, secondary metabolites optimal media for metabolite production. However, identification to the species level is often very difficult due to lack of good identification systems

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and a lot of errors exist in literature [2,12]. Usage of chemotaxonomy is one of the efficacious approaches in HTS programs as both identity and metabolite production can be assessed in one go by a standardised metabolite screening method [1,8,13]. Other techniques can be advantageous in selection of the isolates for the HTS screening, e.g., identification by image analysis [14,15], fast chemical fingerprinting [16–19] and molecular biological method [8,20]. From knowledge of species identity, the biological diversity can be maximised by studying few isolates from many species, rather than just a vast number of unidentified isolates [1,21,22]. The chemotaxonomically approach also allow finding alternative producers of a specific component as well as organisms producing of related components [23,24], e.g., looking at species from similar habitats or the same species series [25].

Since the chemical diversity is very high within the micro-fungi almost all types of chemical structure can be expected in an extract, e.g., small acids, alcohols, ketones, alkaloids, antraquinones and cyclic peptides. To cope with this broad range of chemical structures, most methods are based on reversed-phase liquid chromatography combined with diode array detection (DAD) [26,27] and atmospheric pressure ionisation [electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI)] mass spectrometry (MS) [6,7,9,10,28–31]. Nearly all methods use water–acetonitrile gradient elution on reversed-phase C_{18} and C_8 columns, although methods for very polar and highly ionised components, using perfusion chromatography [32] and hydrophilic interaction chromatography have been described [29,33].

Recently, easy-to-use high resolution orthogonal time-of-flight (oaTOF) mass spectrometers have been introduced boosting the mass precision to better than 5 ppm [34,35] thereby giving an estimate of the molecular composition of each ion. Combining these instruments into liquid chromatography (LC)–UV–MS allows a routine formula estimation along with detection of UV spectra [34,35]. This information greatly limit the number of possible structures from each peak in the chromatograms and also the number of hits in database searches (e.g., in SciFinder, Antibase, MARINLIT and others) [7]. This instrument combination is probably the most efficacious tool for an HTS-chemo-taxonomic screening set-up, with LC–nuclear magnetic resonance (NMR) techniques as an alternative for efficient characterisation of low quantities of chemical analogues [36,37].

An important point is handling the immense quantities of data collected during the LC–UV–MS screening requiring some kind of automatic data handling and archiving [38], automatic aligning of the profiles [39] or multivariate techniques for comparison between samples without the need for full component identification [40,41].

Previously, we have described metabolite micro-scale screening method for fungal identification and classification of species within the genera of *Penicillium*, *Aspergillus*, *Fusarium*, *Alternaria*, *Trichoderma* and *Stachybotrys* [41–47], based on the thin-layer chromatography (TLC) [48], LC–UV [27,49], gas chromatography (GC)–MS–MS [50] and direct electrospray MS [16,17]. Please note that these micro-scale methods are designed for rich media giving a high secondary metabolite yield and a limited medium background.

In this paper we present an updated method utilising LC–UV–MS for quick dereplication of metabolites in fungal extracts supplemented with data from analysis of more than 400 fungal metabolites and mycotoxins standards. The advantage of accurate mass determination is highlighted as well as some of the problems.

2. Experimental

2.1. Chemicals

Gradient-grade methanol (MeOH), acetonitrile and ethyl acetate was obtained from Rathburn (Walkerburn, UK), Riedel-de Haën (Seelze, Germany) and Lab-Scan (Dublin, Ireland), respectively. Analytical pure trifluoroacetic acid (TFA), poly(ethylene glycol) (PEG) 200, 400, 600 and 1000, and isopropanol were obtained from Merck (Darmstadt, Germany). From Sigma (Steinheim, Germany), reserpine, ammonium acetate, formic acid, leucine enkephalin, and the alkylphenone retention index (I) standards [27]: acetophenone, propiophenone, butyrophenone, valerophenone, hexanophenone, octanophenone, decaneophenone, were obtained. The standards for I

determination were diluted in MeOH to 1.2, 2.4, 2.1, 2.1, 2.4, 2.8 and 2.8 m*M*, respectively (giving about equal peak heights in UV). Water was Milli-Q grade (Millipore, Billerica, CA, USA). Reserpine for MS tuning was diluted in acetonitrile–water (1:1, v/v) to 1 μg/ml. The PEG calibration (0.5 μg/ml PEG 200, 1 μg/ml PEG 400, 1.5 μg/ml PEG 600, and 2.5 μg/ml PEG 1000) mixture was dissolved in acetonitrile–water (1:1, v/v) with 2 m*M* ammonium acetate.

2.2. Preparation of metabolite standards

Metabolite standards have been collected over the years [27,51], either from commercial sources or as gifts from different research groups, and therefore only available in micro- to milligram quantities, some only about 50–80% pure. About 30% of the standards have been purchased from Sigma–Aldrich, and a few from Romer Labs. (Union, MO, USA), Calbiochem (San Diego, CA, USA), and ICN (Irvine, CA, USA).

In all cases a few crystals of the standards were dissolved in 1 ml MeOH in a 2-ml vial. Quantification was done on basis of the extinction coefficients (ε) in MeOH [52], unless they were acquired as quantitative reference standards. Absorption was measured in 10-mm quartz cuvettes (Hellma, Müllheim, Germany) on a Lambda 2 UV–Vis spectrophotometer (Perkin-Elmer, Überlingen, Germany). The purity of the standards as quantified by UV, was corrected for impurities based on peak areas of impurities (if present) determined by HPLC–UV, at UV max of the standard. The standards are stored in dry form at −20 °C.

2.3. Preparation of fungal extracts

Fungal cultures were identified by micro and macro morphology accordingly to Samson et al. [53] and cultivated at 25 °C on agar substrates for 7–14 days depending on the genus. All strains are available from the IBT Culture Collection, BioCentrum-DTU, Technical University of Denmark.

Extracts were prepared by a modified version of the micro-extraction method Smedsgaard [49], where the 6-mm plugs were extracted twice in a 2-ml vial for 30 min, first using 1 ml ethyl acetate with 1% formic acid and then using 1 ml isopropanol; the pooled extracts were evaporated in a rotational vacuum concentrator (RVC; Christ Martin, Osterode, Germany). Residue was dissolved in 400 μl methanol, ultrasonicated for 10 min, and filtered through a 0.45-μl PTFE syringe filter (SRI, Eatontown, NJ, USA).

2.4. Instrumentation

All analyses were done on an Agilent HP 1100 liquid chromatograph with a DAD system (Waldbronn, Germany) coupled to a LCT oaTOF mass spectrometer (Micromass, Manchester, UK) with a Z-spray ESI source and a LockSpray probe. Unless other indicated, 1 μl of the dissolved standard was injected on an Agilent Hypersil BDS-C_{18} column with 3 μm particles, 125×2 mm I.D. column with an Agilent 10×2 mm HP Supersphere 100 RP_{18} guard column. The analysis was done at a flow-rate of 0.3 ml/min with a water–acetonitrile gradient, starting at acetonitrile–water (15:85) going to 100% acetonitrile in 40 min, maintaining 100% acetonitrile for 5 min, before returning to the start conditions in 8 min and equilibrating for 5 min [49]. TFA, 50 μl/l, was added to the water. The UV spectra were collected by DAD every 0.4 s from 200 to 700 nm with a resolution of 4 nm.

The MS system was operated in the positive ESI mode and tuned to a resolution >6000 (at half peak height) on the reserpine solution at a flow of 4–100 μl/min infused with a Havard Apparatus 11 syringe pump (Holliston, MA, USA). Calibration of the MS system was subsequently performed on the PEG mixture at a flow of 3–5 μl/m. The capillary was held at 3000 V, cone 1 (skimmer 1) at 30 V (unless other indicated) and cone 2 (skimmer 2) at 6 V. Desolvation temperature was 350 °C during the run at 0.3 ml/min and the source kept at 120 °C. The system was controlled by MassLynx 3.5 (Micromass). The LockSpray was operated with a cone voltage of 35 V spraying a solution of 0.2 μg/ml of leucine enkephalin in acetonitrile–water–formic acid (50:50:0.1) at a flow of 4 μl/min from the syringe pump. The $[M+H]^+$ ion at m/z 556.2771 from leucine enkephalin was used as lockmass (keeping the ion counts below 500).

MS spectra was collected as centroid data from m/z 100 to 900, with a scan time of 1 s and an inter

scan time of 0.1 s. Every third scan was a reference scan from the LockSpray ESI probe, a detailed description of this setup can be found in Wolff et al. [54]. The instrument accuracy performance was validated by analysing a known compound in one of the first analytical runs and often also in the each analytical run if a known compounds was detected. A new calibration was performed if the accurate masses were more than 4–5 ppm off or consistently higher/lower than the calculated mass.

3. Results and discussion

Data from 474 fungal metabolites are collected in Table 1. The table list the metabolite, formula, retention time/retention index calculated as described by Frisvad and Thrane [27], peak asymmetry, and UV and mass spectral data. The ions listed were confirmed by manual mass de-convolution. The peak asymmetry was calculated at 10% peak height from the UV chromatogram. The accurate mass measurements were calculated from spectra obtained in the front or tail of the peak to reduce influence of detector dead time, thus at ion counts below 500. The relative sensitivity index (RSI) of the MS versus the UV (diode array data) was calculated as the peak area of the most intense ion ±0.5 u compared with peak area of the most specific and usually highest absorption trace (±2 nm) as indicated in bold in Table 1.

3.1. Liquid chromatography

The high-performance liquid chromatography (HPLC) separation is a simple adaptation on our previous described HPLC screening method [49], however without trifluoroacetic acid in the acetonitrile to make the gradient more suitable for positive electrospray ionisation, and using a 2 mm I.D. column to improve the resolution and to stay within the optimal flow range of the Z-spray source.

As the alkylphenones are poorly ionised by ESI^+ the UV trace used for detection of these and for calculation of retention index.

About 75% of the components in Table 1 have fairly symmetrical peaks with asymmetries (10% peak height) between 0.8 and 1.7, which is acceptable from a general screening purpose. Compounds without strong polar groups such as the trichothecenes, aflatoxins and their precursors, zeralenons, atranones, etc., all has peak asymmetries within 0.9 to 1.5. Conversely roquefortines and a number of other alkaloids tailed significantly with peak symmmetries of 6–14 even though the Hypersil BDS C_{18} silica is especially deactivated for alkaloids.

The present shows an *I* 20–40 higher in the current system compared with our previously published data [27] (based on a Nucleosil C_{18} column), expect for some alkaloids and amino acid derived compounds that elutes earlier in the new system due to a better deactivated column. If other C_{18} materials than the Hypersil BDS is used, it will be necessary to determine how the *I* of various metabolite groups (especially acids and alkaloids) differs from that of the BDS C_{18}.

The reproducibility of *I* for most compounds were as good ±1–2 *I* (over several years) by our standard LC–DAD method [49] (results not shown). Some alkaloids and amino acid derived compounds, e.g., ochratoxins, roquefortines, AAL toxins and fumonisins, showed a variation in retention index up to ±10–20 *I* due to the interaction with the silanol groups of the column. This was especially pronounced in case of column overload, which occur as some species and isolates produces particularly high quantities of certain metabolites. In extreme cases some alkaloids were found to elute more than 30 *I* to early. High quantities of citric acid or other small acids, acting as ion-pairing components, have in extreme cases resulted in ochratoxin A eluting up to 50 *I* to late (~2 min) compared with a pure standard run.

3.2. LC–MS

Nearly all compounds studied were detected under the ESI conditions used. The dominant ions are listed in Table 1 with LC and UV data. However, in screening methods where long gradients are needed to separate all compounds of interest, some compromises have to be made when selecting ESI source parameters. Therefore, gradients starting with 90–95% water results in poor ionisation of the early eluting analytes due to reduced volatility and high surface tension of the eluent (high temperature

Table 1
Chromatographic properties, and UV and positive electrospray spectra of the investigated metabolites

Metabolite	Formula	Retention time (min)	Retention index	Peak symmetry[a]	UV absorption (nm) in % of UV-max	Mono isotopic mass	Predominant mono isotopic ions in % of base peak	Relative sensitivity factor[b]
Aflatoxins and their precursors								(MS/UV)
Aflatoxicol I	$C_{17}H_{14}O_6$	12.45	880	1.1	208, 252sh[c], 260(30), **332(32)**	314.0790	297	0.1
Aflatoxin B_1	$C_{17}H_{12}O_6$	11.50	859	1.1	200, 224(70), 264(45), 336sh, **364(68)**	312.0634	313	0.2
Aflatoxin B_2	$C_{17}H_{14}O_6$	10.33	834	1.1	200, 222(68), 232sh, 268(48), 336sh, **364(90)**	314.0790	315	0.2
Aflatoxin $B_2\alpha$	$C_{17}H_{14}O_7$	6.60	753	1.4	ND[d] (due to low quantity available)	330.0740	331	–
Aflatoxin G_1	$C_{17}H_{12}O_7$	10.16	830	1.1	200, 220(90), 232sh, 264(40), 336sh, **368(70)**	328.0583	329, 679(10)	0.2
Aflatoxin G_2	$C_{17}H_{14}O_7$	8.97	804	1.1	200, 216(95), 244sh, 264(40), **372(85)**	330.0740	331, 683(12), 394(8)	0.2
Aflatoxin $G_2\alpha$	$C_{17}H_{14}O_8$	5.00	718	1.4	ND (due to low quantity available)	346.0689	347, 276(6)	
Aflatoxin M_1	$C_{17}H_{12}O_7$	7.21	781	1.3	204(100), 228(90), 264(52), 330sh, **360(81)**	328.0583	329, 346(3)	0.3
Austocystin A	$C_{19}H_{13}ClO_6$	21.57	1140	1.3	**248(100)**, 290sh, 304(30), 340(14)	372.0401	373, 436(5)	0.2
Averufin	$C_{20}H_{16}O_7$	25.65	1289	1.5	224(95), **292(100)**, 268(55), 254sh, 322(24), 456(32)	368.0896	369, 399(18)	0.07
5-Methoxysterigmatocystin	$C_{19}H_{14}O_7$	18.02	1028	0.9	200(90), 234sh, **248(100)**, 275sh, 332(42), 380sh	354.0740	355	0.2
Dihydroxysterigmatocystin	$C_{18}H_{14}O_6$	17.70	1018	0.9	206(55), 233sh, **248(100)**, 326(44)	326.0790	327, 390(9)	0.10
Methoxysterigmatocystin	$C_{19}H_{14}O_6$	15.03	944	1.1	204(85), **240(100)**, 312(50)	338.0790	339, 699(30), 402(8)	0.05
Sterigmatocystin	$C_{18}H_{12}O_6$	18.91	1055	0.9	204(75), 235sh, **248(100)**, 328(47)	324.0634	325, 388(5)	0.7
Norsolorinic acid	$C_{20}H_{18}O_7$	31.08	1514	2.3	**236(100)**, 270sh, 282sh, 308(91), 468(43)	370.1053	371	0.0002
Parasiticol	$C_{16}H_{14}O_6$	10.73	842	1.3	**206(100)**, 260(23), 328(28)	302.0790	303, 344(5)	0.1
Trichothecenes[e]								
Nivalenol	$C_{15}H_{20}O_7$	1.27	638	0.9	**220**	312.1209	336, 247(40), 381(30), 189(30), 277(30)	0.002
Fusarenone X	$C_{17}H_{22}O_8$	2.35	661	1.5	**220**	354.1315	247, 229(70), 205(70), 337(70), 355(70), 418(70)	0.005
Deoxynivalenol	$C_{15}H_{20}O_6$	1.54	644	1.2	**220**	296.1260	231, 249(95), 297(60), 203(55)	0.003
3-Acetyldeoxynivalenol	$C_{17}H_{22}O_7$	5.21	723	1.3	**220**	338.1366	231, 213(75), 203(55), 175(50), 279(40), 137(38)	0.011
15-*O*-Acetyl-4-deoxynivalenol	$C_{17}H_{22}O_7$	5.10	721	1.4	**224**	338.1366	261, 361(50), 321(48), 231(42), 361(40)	0.02
Scirpentriol	$C_{15}H_{22}O_5$	1.82	650	1.2	**End**[f]	282.1467	306, 265(35), 217(32), 247(30), 229(20)	0.03
15-Acetoxyscirpenol	$C_{17}H_{24}O_6$	7.40	770	1.4	**End**	324.1573	306, 229(65), 107(30), 247(30)	0.01
Diacetoxyscirpenol	$C_{19}H_{26}O_7$	11.28	854	1.6	**End**	366.1679	307, 389(90), 247(60), 299(55), 349(52)	0.015
3α-Acetyldiacetoxyscirpenol	$C_{21}H_{28}O_8$	15.56	958	1.5	**End**	408.1784	431, 229(50), 247(38), 201(30), 289	0.025
Neosolaniol	$C_{19}H_{26}O_8$	3.19	679	1.4	**End**	382.1628	405, 245(90), 400(60), 215(60), 395(45)	0.02
T-2 Triol	$C_{20}H_{30}O_7$	10.66	841	1.4	**End**	382.1992	145, 215(98), 169(75), 159(72), 187(70)	0.005
HT-2 Toxin	$C_{22}H_{32}O_8$	13.69	908	1.1	**End**	424.2097	263, 245(60), 215(55), 442(30), 197(30)	0.01
T-2 Toxin	$C_{24}H_{34}O_9$	17.06	999	1.4	**End**	466.2203	489, 215(55), 305(45), 484(38), 245(35)	0.001
Iso-T-2 toxin	$C_{24}H_{34}O_9$	17.61	1015	1.8	**End**	466.2203	467, 245(90), 305(70), 215(65), 484(52)	0.02
Acetyl-T-2 toxin	$C_{26}H_{36}O_{10}$	21.12	1125	1.6	**End**	508.2308	531, 287/50), 215(30), 197(25)	0.04
Trichodermin	$C_{17}H_{24}O_4$	16.13	974	1.3	**End**	292.1675	233, 215(65), 293(45), 274(20), 187(30)	0.04
Trichodermol	$C_{15}H_{22}O_3$	9.69	820	1.0	**End**	250.1569	125, 166(85), 187(75), 233(62), 215(59), 314(48), 292(48)	0.005
7-α-Hydroxytrichodermol	$C_{15}H_{22}O_4$	2.59	666	1.4	**End**	266.1518	249, 231(30), 267(20)	0.03
Verrucarol	$C_{15}H_{22}O_4$	2.89	673	1.5	**End**	266.1518	231, 159(70), 249(70), 185(70), 330(30), 308(25)	0.003
4,15-Diacetylverrucarol	$C_{19}H_{26}O_6$	14.15	920	1.2	**End**	350.1729	373, 414(95)	0.015
Trichothecin	$C_{19}H_{24}O_5$	16.29	978	1.5	**216**	332.1624	211, 229(70), 201(65), 159(60), 333(20)	0.001
Trichothecolone	$C_{15}H_{20}O_4$	3.63	689	1.6	**228**	264.1362	211, 175(30), 123(30), 229(25), 306(10)	0.005

Table 1. Continued

Metabolite	Formula	Retention time (min)	Retention index	Peak symmetry[a]	UV absorption (nm) in % of UV-max	Mono isotopic mass	Predominant mono isotopic ions in % of base peak	Relative sensitivity factor[b]
Macrocyclic trichothecens and precursors[e]								
Isosatratoxin F	$C_{29}H_{34}O_{10}$	15.63	960	1.4	End(100), **252(42)**, 286sh	542.2152	543, 560(58), 249(42), 525(39), 231(30)	0.2
Roridin A	$C_{29}H_{40}O_9$	16.29	978	1.4	**264**	532.2672	555, 249(76), 231(36), 550(18), 533(12)	0.03
Roridin E	$C_{29}H_{38}O_8$	20.60	1107	1.7	**224(100)**, 264(80)	514.2567	532, 361(70), 515(18)	0.3
Roridin H	$C_{29}H_{36}O_8$	24.33	1238	1.8	**224(100)**, 260(72)	512.2410	513, 530(95), 359(32)	0.07
Roridin L-2	$C_{29}H_{38}O_9$	13.37	900	1.4	200(85), **260(100)**	530.2516	531, 283(75), 513(50), 249(45), 231(20)	0.05
Satratoxin G	$C_{28}H_{32}O_{11}$	13.43	901	1.5	200(100), **256(66)**	544.1945	545, 527(80), 249(75), 231(50), 562(48)	0.08
Satratoxin H	$C_{29}H_{36}O_9$	14.14	920	1.4	200(85), **232**(100), 265sh	528.2359	529, 511(25), 546(20), 551(15), 281(10), 263(10)	0.02
Trichoverrin A	$C_{29}H_{40}O_9$	14.20	922	1.3	224(82), **260(100)**	532.2672	361, 550(40), 555(32), 249(10), 231(8)	0.2
Trichoverrin B	$C_{29}H_{40}O_9$	14.10	919	1.3	224(88), **260(100)**	532.2672	361, 550(40), 555(32), 249(10), 231(8)	0.1
Trichoverrol A	$C_{23}H_{32}O_7$	10.16	830	1.4	200(50), **264(100)**	420.2148	249, 231(35), 290(25), 438(20), 403(15), 443(12)	0.1
Trichoverrol B	$C_{23}H_{32}O_7$	9.85	823	1.4	200(50), **264(100)**	420.2148	249, 231(40), 443(40), 290(18), 438(15), 466(15)	0.2
Verrucarin A	$C_{27}H_{34}O_9$	16.40	981	1.4	**260**	502.2203	249, 231(85), 555(55), 525(50), 193(30)	0.005
Verrucarin J	$C_{27}H_{32}O_8$	21.52	1138	1.3	**220(100)**, 264(71)	484.2097	485, 502(82), 343(40), 373(18), 231(15)	0.09
Ochratoxins								
Ochratoxin A	$C_{20}H_{18}NO_6Cl$	20.33	1098	1.3	**216(100)**, 250sh, 332(20)	403.0823	404, 358(22)	0.1
Ochratoxin B	$C_{20}H_{19}NO_6$	15.47	956	1.4	**216(100)**, 248sh, 320(20)	369.1212	370, 324(35), 223(29), 205(15)	0.09
Ochratoxin α	$C_{11}H_9ClO_5$	5.60	731	1.4	**216(100)**, 235sh, 248sh, 336(22)	256.0139	257, 239(22)	0.09
Ochratoxin A-ethyl ester	$C_{22}H_{22}NO_6Cl$	24.33	1238	1.3	**216(100)**, 250sh, 332(20)	431.1136	432, 358(44), 386(40)	0.3
Ochratoxin A-methyl ester	$C_{21}H_{20}NO_6Cl$	22.49	1171	1.4	**216(100)**, 250sh, 332(20)	417.0979	418, 358(40), 386(30)	0.3
Ochratoxin B-ethyl ester	$C_{22}H_{23}NO_6$	20	1088	1.3	**218(100)**, 247sh, 320(20)	397.1525	398, 324(40), 352(25)	0.4
Ochratoxin B-methyl ester	$C_{21}H_{21}NO_6$	19.41	1070	1.3	**218(100)**, 247sh, 320(20)	383.1369	384, 324(40), 352(25)	0.3
Ochratoxin α-methyl ester	$C_{13}H_{12}ClO_5$	18.93	1055	1.4	**216(100)**, 250sh, 336(20)	284.0452	257, 239(40), 285(30)	0.2
Ochratoxin α-methyl ester	$C_{12}H_{10}ClO_5$	16.16	974	1.4	**216(100)**, 250sh, 336(20)	270.0295	257, 239(40), 271(30)	0.1
Sphinganin myotoxins								–
AAL toxin TA_1	$C_{25}H_{47}NO_{10}$	13.33	899	1.5	ND	521.3200	522	–
AAL toxin TA_2	$C_{25}H_{47}NO_{10}$	13.63	906	1.5	ND	521.3200	522	–
AAL toxin TB_1	$C_{25}H_{47}NO_9$	16.16	974	1.5	ND	505.3251	506	–
AAL toxin TB_2	$C_{25}H_{47}NO_9$	16.57	985	1.5	ND	505.3251	506	–
Fumonisin B_1	$C_{34}H_{59}NO_{15}$	17.40	1009	1.5	ND	721.3885	722	–
Fumonisin B_2	$C_{34}H_{59}NO_{14}$	22.40	1168	1.5	ND	705.3936	706	–
Cytohalasins								
Chaetoglobosin A	$C_{32}H_{36}N_2O_5$	19.08	1060	1.3	End(90), **220(100)**, 276(17)	528.2624	511, 529(55), 493(14), 552(13)	0.03
Chaetoglobosin C	$C_{32}H_{36}N_2O_5$	21.39	1134	0.9	**220(100)**, 252(25), 280sh, 290sh	528.2624	529, 551(10), 511(8)	0.03
Cytochalasin A	$C_{29}H_{35}O_5N$	20.00	1088	1.1	**End**, 230sh	477.2515	478, 460(5)	0.2
Cytochalasin B	$C_{29}H_{37}O_5N$	15.40	954	1.3	**End**	479.2672	480, 462(13), 444(6)	0.3
Cytochalasin C	$C_{30}H_{37}O_6N$	18.34	1038	1.4	**End**	507.2621	430, 490(45), 508(45)	0.08
Cytochalasin D	$C_{30}H_{37}O_6N$	15.91	968	1.5	**End**	507.2621	430, 490(45), 508(45)	0.06
Cytochalasin E	$C_{28}H_{33}O_7N$	18.09	1030	1.1	**End**	495.2257	434(100), 513(75), 416(75), 496(30), 478(25)	0.1
Cytochalasin H	$C_{30}H_{39}NO_5$	15.61	960	1.5	**End**	493.2828	476, 416(95), 434(70), 494(25), 398(20)	0.06
Cytochalasin J	$C_{28}H_{37}NO_4$	11.94	869	1.2	**End**	451.2723	434, 416(75), 416(70), 452(15), 398(15)	0.04
Dihydrocytochalasin B	$C_{29}H_{39}NO_5$	19.30	1067	1.4	**End**	481.2828	482, 464(98), 446(12)	0.06
Dihydrocytohalasin B γ lactone	$C_{29}H_{39}NO_5$	19.02	981	1.5	**End**	481.2828	446, 482(98), 464(90)	0.2

Zeralenons								
α-Zearalanol	$C_{18}H_{26}O_5$	15.82	965	1.4	**216(100)**, 264(52), 300(20)	322.1780	305, 287(30), 261(10), 207(8)	0.02
β-Zearalanol	$C_{18}H_{26}O_5$	13.65	907	1.4	**206(100)**, 260(29), 287sh, 301sh	322.1780	305, 287(25), 167(10), 277(10)	0.03
Zearalanone	$C_{18}H_{24}O_5$	17.83	1022	1.5	**216(100)**, 264(52), 300(20)	320.1624	303, 321(22), 277(5)	0.07
α-Zearalenol	$C_{18}H_{24}O_5$	15.74	963	1.5	**236(100)**, 276(45), 316(18)	320.1624	285, 303(55), 267(20), 257(10)	0.02
β-Zearalenol	$C_{18}H_{24}O_5$	13.96	915	1.4	**240(100)**, 268(47), 308(14)	320.1624	285, 267(52), 229(40), 303(40)	0.004
Zearalenone	$C_{18}H_{22}O_5$	18.05	1029	1.4	**236(100)**, 272(45), 318(18)	318.1467	301, 283(92), 319(35)	0.03
Roquefortines, ergot amines and related alkaloids								
Agroclavine-I	$C_{16}H_{18}N_2$	17.00	997		**228(100)**, 280(28)	238.1470	239, 280(10)	3
Auranthine	$C_{19}H_{14}N_4O_2$	10.51	838	1.2	**228(100)**, 268(23), 278sh, 312(10), 322sh	330.1117	331, 372(42)	0.2
Aurantiamine (alkaloid 302)	$C_{16}H_{22}N_4O_2$	10.49	837	4.8	232(53), **320(100)**	302.1743	303	0.4
Aurantioclavine	$C_{15}H_{18}N_2$	14.30	924	13	End(88), **224(100)**, 288(22)	226.1470	210, 227(62), 171(15)	0.3
Chanoclavine-I	$C_{16}H_{20}ON_2$	8.59	796	10	End(87), **224(100)**, 280(22)	256.1576	257, 226(60), 208(20), 168(18)	0.2
Costaclavine	$C_{16}H_{20}N_2$	17.00	997	5	**208(100)**, 224sh(30), 268(5), 280sh	240.1626	241	0.2
Cyclopenin	$C_{17}H_{14}N_2O_3$	11.60	861	2.4	End(95), **212(100)**, 290(6)	294.1004	177, 295(80), 146(22), 336(10)	0.05
Cyclopenol	$C_{17}H_{14}N_2O_4$	6.20	744	3	**End(100)**, 214sh, 284(7)	310.0954	311, 177(48), 621(12)	0.02
Cyclopeptin	$C_{17}H_{16}N_2O_2$	12.05	871	1.3	**216(100)**, 292(5)	280.1212	281, 322(10)	0.05
Dihydroergotamin	$C_{33}H_{37}N_5O_5$	18.60	1045	7.8	End(100), **220(78)**, 280(14)	583.2795	584, 566(5)	0.4
Elymoclavine	$C_{16}H_{18}ON_2$	5.34	726	14	End(94), **220(100)**, 280(21)	254.1419	255	0.2
Epoxyagroclavine-I	$C_{16}H_{18}ON_2$	10.00	827	9	**224(100)**, 280(20)	254.1419	255, 315(12)	1
Ergocristine	$C_{35}H_{39}N_5O_5$	25.10	1332	2	End(100), **240(48)**, 320(20)	609.2951	610, 592(14), 575(11)	0.1
Ergometrin	$C_{19}H_{23}N_3O_2$	5.45	728	8	End(100), **228(94)**, 314(36)	325.1790	326, 283(6)	0.03
Ergotamin	$C_{33}H_{35}N_5O_5$	19.60	1127	6	**End(100)**, 238sh(40), 320(18)	581.2638	582, 564(18)	0.6
Fumigaclavine B	$C_{16}H_{20}ON_2$	6.60	753	12	**224(100)**, 280(19)	256.1576	257	0.4
Fumigaclavine C	$C_{23}H_{30}O_2N_2$	21.40	1134		**226(100)**, 280(19)	366.2307	367	0.4
Marcfortine A	$C_{28}H_{35}N_3O_4$	19.59	1076	8	**224(100)**, 256sh, 287sh	477.2628	478, 450(7), 462(4)	4
Marcfortine B	$C_{27}H_{33}N_3O_4$	17.39	1009	6	203sh(70), **226(100)**, 256sh, 288sh	463.2471	464, 436(4), 505(3)	2
Meleagrin	$C_{23}H_{23}N_5O_4$	18.90	1055	14	End(100), 228(71), 284sh, **328(72)**	433.1750	434, 403(50)	2
Oxalin	$C_{24}H_{25}N_5O_4$	21.60	1141	7	End(100), 228(70), 284sh, **328(72)**	447.1907	448, 417(45)	1
Pyroclavine	$C_{16}H_{20}N_2$	14.81	938	7	**224(100)**, 280(22)	240.1626	241, 282(5)	2
Roquefortine A	$C_{18}H_{22}O_2N_2$	13.91	914	12	**224(100)**, 280(18)	298.1681	299	1
Roquefortine B	$C_{16}H_{20}ON_2$	7.41	771	12	**224(100)**, 280(19)	256.1576	257, 239(58), 197(8)	0.1
Roquefortine C	$C_{22}H_{23}N_5O_2$	20.50	1104	17	**204(100)**, 236(43), 304(79)	389.1852	390	0.6
Roquefortine D	$C_{22}H_{25}N_5O_2$	6.09	742	10	**220(100)**, 288(47), 302(47)	391.2008	322, 193(35), 344(5)	0.03
Rugulosuvine	$C_{20}H_{19}N_3O_2$	10.24	832	2	**224(100)**, 280(18)	333.1477	334, 375(8)	0.06
Rugulovasine A and B	$C_{16}H_{16}N_2O_2$	8.43	793	10	**220(100)**, 292(15)	268.1212	269, 251(10)	0.2
Secoclavine	$C_{16}H_{20}N_2$	20.40	1100	5	**224(100)**, 280(22)	240.1626	210, 241(70)	0.6
α-Ergocryptin	$C_{32}H_{41}N_5O_5$	19.20	1064	10	**End(100)**, 238sh(48), 318(18)	575.3108	576, 558(48)	1
Atranone and their precursors								
Atranone A	$C_{24}H_{32}O_6$	17.92	1025	1.3	End(100), **224sh(65)**	416.2199	399, 417(72), 381(25), 458(22)	0.2
Atranone B	$C_{25}H_{34}O_7$	20.07	1090	1.3	End(100), **230sh(65)**	446.2305	429, 447(20)	0.1
Atranone E	$C_{24}H_{34}O_4$	21.52	1138	1.5	End(100), **236(79)**	386.2457	387, 428(42), 341(10)	0.4
Atranone F	$C_{24}H_{32}O_7$	19.35	1068	1.5	End(100), **232sh(50)**	432.2148	433, 865(85), 355(22), 474(15)	0.4
Atranone H	$C_{24}H_{32}O_8$	18.00	1027	1.4	**End**	448.2097	431, 387(12), 285(11), 243(10)	0.08
Atranone J	$C_{23}H_{32}O_6$	20.48	1103	1.4	**End**	404.2199	345, 387(91), 369(40), 327(26)	0.1
6-Hydroxydolaballa-3,7,12-trien-14-one	$C_{20}H_{30}O_2$	16.90	994	1.3	End(100), **240(70)**	302.2246	219, 303(95), 344(20)	0.1
3,4-Epoxy-6-hydroxy-dolabella-7,12-diene-one	$C_{20}H_{30}O_3$	14.64	934	1.3	End(100), **230(70)sh**	318.2195	319, 301(80),	0.09

Table 1. Continued

Metabolite	Formula	Retention time (min)	Retention index	Peak symmetry[a]	UV absorption (nm) in % of UV-max	Mono isotopic mass	Predominant mono isotopic ions in % of base peak	Relative sensitivity factor[b]
Tremorgens								
Fumitremorgen B	$C_{27}H_{33}O_5N_3$	20.64	1163	1.7	End(100), **228(94)**, 278(18), 296(21)	479.2420	462, 479(10), 480(9), 512(5)	1
Lolitrem B	$C_{42}H_{55}NO_7$	30.70	1497	1.7	End(38), **264(100)**, 288sh, 338sh	685.3979	686, 620(19), 576(15), 602(15)	0.3
Lolitriol	$C_{37}H_{49}NO_7$	21.50	1138	1.8	End(38), **264(100)**, 288sh, 338sh	619.3509	620, 510(15)	0.3
Territrem A	$C_{28}H_{30}O_9$	19.41	1070	1.3	**220(100)**, 340(48)	510.1890	511	0.3
Territrem B	$C_{29}H_{34}O_9$	18.70	1048	1.6	**220(100)**, 332(48)	526.2203	527	0.2
Territrem C	$C_{28}H_{32}O_9$	15.91	968	1.4	**220(100)**, 344(50)	512.2046	513	0.6
Penitrem A	$C_{37}H_{44}O_6NCl$	25.50	1283	1.6	**236(100)**, 300(30)	633.2857	634, 616(50), 588(25), 633(25)	0.1
Penitremone A	$C_{37}H_{45}O_6N$	24.71	1253	1.4	260(100), 286sh, 336sh	599.3247	600, 514(71), 582(17), 532(8)	0.06
1′-Acetoxypaxillin	$C_{29}H_{35}O_5N$	27.02	1343	1.5	**232(100)**, 280(22)	477.2515	130, 418(98), 182(60), 400(45), 478(30)	0.002
Deoxypaxillin	$C_{27}H_{33}O_3N$	27.39	1357	1.4	232(100), 252sh, 280(20)	419.2460	402, 182(12), 130(10), 362(8)	0.01
Paxillin	$C_{27}H_{33}O_4N$	24.13	1230	1.6	232(100), 250sh, 280(22)	435.2410	418, 436(30)	0.05
α-Paxitriol	$C_{27}H_{35}NO_4$	21.35	1132	1.5	230(100), 280(25)	437.2566	130, 402(45), 182(28), 437(13), 438(12), 429(10)	0.006
β-Paxitriol	$C_{27}H_{35}NO_4$	19.96	1087	1.5	230(100), 280(25)	437.2566	130, 402(70), 182(30), 428(20), 501(20)	0.007
Janthitrem B	$C_{37}H_{47}O_5N$	20.29	1097	1.1	End(80), 264(100), 332(60)	585.3454	510, 586(75), 568(56)	0.01
Peptides								
Alamethicin[g]	$C_{92}H_{150}N_{22}O_{25}$	25.98	1302	1.8	End	1963.1142	774, 1189(69), 982(7), 595(4), 1964(2)	1
α-Amanitin[g]	$C_{39}H_{54}N_{10}O_{14}S$	1.63	645	1.4	200(100), 216sh, 240sh, 304(29)	918.3542	919, 901(10)	0.03
Antimycin A1[h]	$C_{28}H_{40}N_2O_9$	31.57	1536	2.7	**228(100)**, 320(18)	548.2734	265, 549(22), 237(5), 571(5)	0.5
Antimycin A2[h]	$C_{27}H_{38}N_2O_9$	29.92	1463	2.7	**228(100)**, 320(18)	534.2577	265, 535(18), 557(8), 237(5)	0.5
Antimycin A3[h]	$C_{26}H_{36}N_2O_9$	28.10	1384	2.6	**228(100)**, 320(18)	520.2421	265, 521(12), 237(5), 543(4)	0.5
Antimycin A4[h]	$C_{25}H_{34}N_2O_9$	26.34	1316	2.6	**228(100)**, 320(14)	506.2264	265, 507(14), 237(8), 529(6)	0.5
Antimycin A5[h]	$C_{24}H_{32}N_2O_9$	24.83	1257	3.0	End(100), 240(45)	492.2108	265, 493(7), 515(3)	0.2
Apicidin	$C_{34}H_{49}N_5O_6$	21.60	1141	1.0	End(100), **224(88)**, 280(10), 288(12)	623.3683	624, 646(25), 594(5)	0.3
Cyclo(Phe-Ser)	$C_{12}H_{14}N_2O_3$	1.52	643	1.4	**End(100)**-broad, 256(3)	234.1004	235, 207(45), 120(18)	0.01
Cyclosporin[g]	$C_{62}H_{111}N_{11}O_{12}$	30.72	1498	1.2	**End**	1201.8414	1202, 1219(76), 601.9(20dc[i]), 510(2)	0.6
Distamycin A[h]	$C_{22}H_{27}N_9O_4$	8.40	792	3	200(75), 236(80), **308(100)**	481.2186	482	0.150
Enniatin A1	$C_{35}H_{61}N_3O_9$	36.19	1817	2.5	ND	667.4408	685, 668(40)	–
Enniatin A2	$C_{36}H_{63}N_3O_9$	38.62	1925	2.5	ND	681.4564	699, 682(32)	–
Enniatin B	$C_{33}H_{57}N_3O_9$	32.36	1359	2.4	ND	639.4095	657, 640(50)	–
Enniatin B1	$C_{34}H_{59}N_3O_9$	34.32	1734	2.7	ND	653.4251	671, 654(45)	–
Malformin A1	$C_{23}H_{39}O_5N_5S_2$	16.49	983	1.5	**End**	529.2393	530, 552(22)	4
Malformin A2	$C_{22}H_{37}O_5N_5S_2$	14.75	937	1.5	**End**	515.2236	516, 538(30)	0.6
Malformin B1	$C_{23}H_{39}O_5N_5S_2$	16.90	994	1.4	**End**	529.2393	530, 552(40)	0.9
Malformin B2	$C_{23}H_{39}O_5N_5S_2$	14.07	918	1.4	**End**	529.2393	530, 552(40)	1
Malformin C	$C_{23}H_{39}O_5N_5S_2$	17.01	997	1.5	**End**	529.2393	530, 547(12), 552(5)	0.8
Phalloidin	$C_{35}H_{48}N_8O_{11}S$	6.20	415	1.4	End, **220(80)**, 292(30)	788.3163	789, 753(20), 771(10)	0.1
Valinomycin[g,h]	$C_{54}H_{90}N_6O_{18}$	40.56	1932	2	**End**	1110.6312	1128, 1111(5)	2.5
Others								
2-(4-Hydroxyazobenzene) benzoic acid	$C_{13}H_{10}N_2O$	13.81	911	1.5	End(90), 248(55), 360(100)	210.0793	225, 243(28), 197(8)	0.3
2,4,6-Trihydroxytoluene	$C_7H_8O_3$	8.00	783	1.9	**212(100)**, 256(71), 324(20)	140.0473	ND	–
2,5-Dihydroxybenzoic acid	$C_7H_6O_4$	1.69	282	0.8	**208(100)**, 232sh(30), 324(18)	154.0266	403, 264(17), 254(10)	0.003

3,5-Dihydrotoluene	$C_7H_8O_2$	2.90	673	1.3	**End(100)**, 220sh, 272(8)	124.0524	125, 166(28)	0.01
3,7-Dimethyl-8-hydroxy-6-methoxy-isochroman	$C_{12}H_{16}O_3$	12.15	873	1.4	**End(100)**, 223sh(20), 284(8)	208.1099	209, 191(30), 207(28), 179(25)	0.12
3-Methylsalicylic acid	$C_8H_8O_3$	11.15	852	0.7	**208(100)**, 240(22), 308(11)	152.0473	399[j]	0.003
5-Methylbenzene-1,2,3 triol	$C_7H_8O_3$	14.73	936	1.2	**End(100)**, 217sh, 284(8)	140.0473	253, 294(20), 311(18)	1
6-Methylcitreoisocumarin	$C_{15}H_{16}O_6$	11.87	867	1.4	**244(100)**, 258sh, 278(13), 288sh, 328(14)	292.0947	233, 293(54), 275(64), 316(12)	0.07
Abscisic acid	$C_{15}H_{20}O_4$	9.56	817	1.4	**264**	264.1362	247, 229(50), 201(30), 328(25)	0.02
2-Acetyl-4(3H)-quinazolone	$C_{10}H_8O_2N_2$	6.70	755	1.1	**204(100)**, 232(88), 304(40)	188.0586	147, 189(75)	0.02
α-Acetyl-γ-methyltetronic acid	$C_7H_8O_4$	0.83	628	1.9	231(95), **263(100)**	156.0423	139, 157(90), 198(50)	0.006
Aflatrem	$C_{32}H_{39}O_4N$	30.49	1488	1.5	**232(100)**, 284(30)	501.2879	502, 444(11), 534(5)	0.2
Alizarin	$C_{14}H_8O_4$	14.60	933	1.4	228sh, **248(100)**, 280(68), 328(14), 432(26)	240.0423	241, 575(85)	0.02
Altenuene	$C_{15}H_{16}O_6$	9.83	823	1.1	**240(100)**, 280(36), 320(18)	292.0947	257, 275(95), 293(65)	0.02
Alternariol	$C_{14}H_{10}O_5$	12.33	877	1.6	204(50), **256(100)**, 288(20), 300(20), 340(23)	258.0528	259, 300(10)	0.009
Alternariol-methyl ether	$C_{15}H_{12}O_5$	17.80	1021	1.4	204(50), **256(100)**, 288(20), 300(20), 340(23)	272.0685	273, 314(5)	0.05
Altersolanol A	$C_{16}H_{16}O_8$	2.90	673	1.0	**220(100)**, 268(41), 430(12)	336.0845	301, 273(70), 319(15), 337(12)	0.02
Altertoxin I	$C_{20}H_{16}O_6$	11.93	868	1.3	216(74), **260(100)**, 284(42), 356(14)	352.0947	317, 353(32), 335(28), 394(6)	0.01
Amphotericin B[h]	$C_{47}H_{73}NO_{17}$	21.39	1134	0.3	228(10), 340(25), 364(52), 384(92), **408(100)**	923.4879	906, 924(68), 761(23), 453(18), 743(20)	0.02
Anacine	$C_{18}H_{22}N_4O_3$	9.56	817	1	202(95), **228(100)**, 272(29), 308(12), 316sh	342.1692	326, 298(75), 343(30), 365(15), 406(15)	0.04
Anhydrofusarubin	$C_{15}H_{12}O_6$	21.45	1136	2	End(100), **236(88)**, 288(87), 348sh, 540(47)	288.0634	289, 330(4)	0.2
p-Anisaldehyde	$C_8H_8O_2$	8.68	798	1.2	End(80), 220(68), **284(100)**	136.0524	137, 178(65), 109(55)	0.0004
Antibiotic Y	$C_{15}H_{10}O_8$	13.37	900	14	204(78), 216(78), **244(100)**, 280(95), 348(75), 364(82)	318.0376	319, 287(25), 382(8)	0.5
Arabenoic acid (Verrucolone)	$C_6H_{10}O_4$	1.47	642	1.4	**240**	146.0579	129, 117(22), 103(20), 157(20)	0.008
Ascochitine	$C_{15}H_{16}O_5$	18.75	1050	8.1	220(81), 262sh, **280(100)**, 326(15), 242(15), 416(38)	276.0998	259, 277(95)	0.5
Aspergillic acid	$C_{12}H_{20}O_2N_2$	13.02	892	2	228(80), **324(100)**	224.1525	209, 250(10)	0.2
Aspergillic acid-polymer[k]	$C_{12}H_{20}O_2N_2$	40.00	1908	2	224(100), **316(100)**	224.1525	697	0.2
Asperthecin	$C_{15}H_{10}O_8$	10.00	827	2.2	End(75), 236(88), **260(100)**, 286(55), 316(36), 484(56), 506sh	318.0376	319	0.002
Asteltoxin	$C_{23}H_{30}O_7$	14.10	919	2	272(90), **368(100)**	418.1992	419, 837(35)	0.3
Asterric acid	$C_{17}H_{16}O_8$	14.81	938	1.4	**212(100)**, 252(30), 316(16)	348.0845	331, 299(85), 287(40), 371(20)	0.04
Austamide	$C_{21}H_{21}O_3N_3$	11.94	869	1.5	**232(100)**, 264sh(45), 396(8)	363.1583	364, 427(8)	0.4
Austdiol	$C_{12}H_{12}O_5$	1.93	652	1.4	204(55), 256(70), **380(100)**	236.0685	237, 177(30), 259(25), 300(15)	0.03
Baccatin III	$C_{31}H_{38}O_{11}$	13.65	744	1.4	End(100), **232(50)**	586.2414	604, 345(95), 327(74), 405(69), 527(55), 587(40)	0.05
Barnol	$C_{10}H_{14}O_3$	10.79	844	1.3	**204(100)**, 222sh, 272(4)	182.0943	165, 183(60), 18(50)	0.002
Beauvericin	$C_{45}H_{57}N_3O_9$	31.02	1511	7.7	**204**	783.4095	784, 801(97), 806(20)	0.6
1,3-Benzendiol	$C_6H_6O_2$	1.80	649	1.4	End(100), 216sh, **276(40)**	110.0368	111, 152(50), 134(5)	0.001
Benzoic acid	$C_7H_6O_2$	6.20	744	1.3	**228(60)**, 272(4)	122.0368	164, 380(58), 123(30)	0.0001
Bikaverin	$C_{20}H_{14}O_8$	20.75	1112	18	**212(100)**, 252(20)	382.0689	383	0.5
Bis-dethio-bis(methylthio)-gliotoxin	$C_{15}H_{20}N_2O_4S_2$	10.66	612	1.3	**End(100)**, 268(20)	356.0865	243, 215(71), 261(60), 233(59), 309(40)	0.1
Bostrycin	$C_{16}H_{16}O_8$	3.95	696	1.4	**228(100)**, 304(30), 482sh, 540(26), 536sh	336.0845	301, 319(87), 273(30), 337(25)	0.04
Bostrycoidin	$C_{15}H_{11}NO_5$	16.90	994	10	204(96), **252(100)**, 324(21), 472sh, 492(29), 526sh	285.0637	286, 327(12)	0.4
Brassicasterol	$C_{28}H_{46}O$	48.70	2292	2.5	**End**	398.3549	381, 255(31), 397(10)	0.009
Brefeldin A	$C_{16}H_{24}O_4$	12.70	885	1.5	**End**-broad to 270 nm	280.1675	245, 199(40), 263(35), 281(30), 322(20), 561(30)	0.04
Brevianamide A	$C_{21}H_{23}N_3O_3$	10.29	833	1.3	**232broad(100)**, 262sh, 408(13)	365.1739	366, 407(30), 731(30)	0.2
Butenolide	$C_6H_7O_3N$	1.27	638	1.0	**End**	141.0426	100, 141(10), 142(6)	0.003
Byssochlamic acid	$C_{18}H_{20}O_6$	21.23	1183	1.4	**204(100)**, 352(58)	332.1260	350, 371(58), 396(22)	0.03
Caffeic acid	$C_9H_8O_4$	2.00	653	1.3	216(78), 240(61), 302sh, **324(100)**	180.0423	163, 181(9), 222(9)	0.011
Caffeine	$C_8H_{10}N_4O_2$	1.71	647	1.6	**208(100)**, 230sh, 272(65)	194.0804	195, 236(18)	0.03

Table 1. Continued

Metabolite	Formula	Retention time (min)	Retention index	Peak symmetry[a]	UV absorption (nm) in % of UV-max	Mono isotopic mass	Predominant mono isotopic ions in % of base peak	Relative sensitivity factor[b]
Calphostin C	$C_{44}H_{38}O_{14}$	24.66	1314	8	**224(100)**, 268(50), 476(41), 543(20), 584(20)	790.2262	791	2
Canadensolide	$C_{11}H_{14}O_4$	13.03	892	1.1	**204**	210.0892	175, 193(40), 147(38), 211(15)	0.010
Candidusin C	$C_{21}H_{18}O_6$	17.67	1017	1.2	**216(100)**, 238sh(68), 280(53),296(50), 332(70)	366.1103	367, 414(10), 335(10)	0.04
Canescin	$C_{15}H_{14}O_7$	13.00	892	1.4	**248(100)**, 280(12), 320(11)	306.0740	289, 229(89), 275(10), 257(10), 343(5)	0.03
Carlosic acid	$C_{10}H_{12}O_6$	1.26	637	1.2	**232(100)**, 264(94), 316sh, 408(8)	228.0634	211, 193(60), 123(50), 243(45),	0.01
Carolic acid	$C_9H_{10}O_4$	1.30	638	1.6	232(85), **264(100)**	182.0579	183, 165(32), 224(10)	0.03
Catenarin	$C_{15}H_{10}O_6$	22.70	1178	3	**232(100)**, 256(50), 276(52), 302(32), 464sh, 492(42), 520sh	286.0477	287	0.008
Chaetocin	$C_{30}H_{28}O_6N_6S_4$	17.92	1025	1.3	**204(100)**, 234sh, 300(9)	696.0953	697, 348(60), 286(20)	0.002
Chetomin	$C_{31}H_{30}O_6N_6S_4$	19.30	1067	1.3	**End(100)**, 218sh, 286sh(13)	710.1110	298, 348(80), 645(61), 733(52), 647(51), 711(50)	0.004
Chromanol 1	$C_{16}H_{18}O_6$	13.92	914	1.2	**220(100)**, 268(47)	306.1103	271, 289(30), 307(8)	0.1
Chromanol 2	$C_{16}H_{18}O_6$	13.19	896	1.3	**220(100)**, 268(50)	306.1103	271, 289(45), 307(9)	0.06
Chromanol 3	$C_{16}H_{20}O_7$	9.85	823	1.3	**220(100)**, 268(48)	324.1209	231, 249(11), 389(8)	0.08
Chrysazin	$C_{14}H_8O_4$	20.84	1115	0.9	**224(100)**, 252(88), 284sh, 428broad(48)	240.0423	241, 282(10)	0.0001
Chrysogine	$C_{10}H_{10}O_2N_2$	2.62	667	1.6	End(85), **228(100)**, 264(22), 304(15)	190.0742	173, 191(96)	0.08
Chrysophanol	$C_{15}H_{10}O_4$	23.98	1224	2	**224(100)**, 256(65), 280sh, 288sh, 43broad2(30)	254.0579	255, 296(40)	0.004
Cinnamic acid	$C_9H_8O_2$	10.62	840	1.2	204(64), 216(65), **276broad(100)**	148.0524	131, 149(7)	0.008
Circumdatin A	$C_{21}H_{19}N_3O_5$	13.92	914	1.4	**204(100)**, 236(53), 290sh, 356(16)	393.1325	394	0.5
Circumdatin B	$C_{20}H_{17}N_3O_4$	12.31	877	1.3	End(85), **248(100)**, 280(28), 340(12)	363.1219	364, 405(5)	0.4
Circumdatin C	$C_{17}H_{13}N_3O_3$	9.36	813	1.1	**232(100)**, 272(30), 302(13), 310(12), 322SH	307.0957	308, 349(20)	0.2
Citreoisocumarin	$C_{14}H_{14}O_6$	6.88	759	1.0	**244(100)**, 258sh, 275(15), 286sh, 328(13)	278.0790	219, 261(50), 279(29), 301(12)	0.01
Citreomontanin	$C_{23}H_{28}O_3$	33.35	1614	1.5	232(40), 268(39), 330(35), **412(100)**	352.2038	353, 297(8), 416(7), 733(55), 711(40)	1
Citreoviridin A	$C_{23}H_{30}O_6$	17.01	997	1.2	204(30), 236(20), 296(50), **388(100)**	402.2042	403	0.003
Citreoviridin X	$C_{23}H_{30}O_7$	15.70	962	1.3	216(25), 272(81), **372(100)**	418.1992	419, 837.8(50), 275(40), 693(40)	0.2
Citrinin	$C_{13}H_{14}O_5$	12.31	877	2.0	**216(100)**, 242sh, 328(40)	250.0841	251, 233(20)	0.3
Citromycetin	$C_{14}H_{10}O_7$	1.32	639	1.0	**212(100)**, 256(53), 300(35), 368(55)	290.0427	273, 291(90)	0.03
Cladofulvin	$C_{30}H_{18}O_{10}$	22.60	1175	3	End(80), 232(95), **268(100)**, 294sh, 448(44)	538.0900	539	0.01
Cladosporin	$C_{16}H_{20}O_5$	15.94	969	1.4	**216(100)**, 268(65), 300(23)	292.1311	293, 275(25), 231(10), 231(11), 257(10)	0.09
Clerocidin	$C_{20}H_{28}O_5$	13.60	906	4.5	**236**	348.1937	331, 313(90), 408(65), 349(50), 390(50), 295(45)	0.01
Communesin A	$C_{28}H_{32}N_4O_2$	21.67	1143	2.5	**204(100)**, 250(18), 268(20)	456.2525	457, 385(12)	6
Communesin B	$C_{32}H_{36}N_4O_2$	28.54	1402	2.0	**204(100)**, 272(90)	508.2838	509	11
Compactin	$C_{23}H_{34}O_5$	23.21	1195	1.5	228sh, **236(100)**, 242sh	390.2406	271, 185(88), 229(75), 391(68), 412(42)	0.04
Culmorin	$C_{15}H_{26}O_2$	16.33	979	1.1	**End**	238.1933	203, 221(78), 177(35), 262(14)	8
Curvularin	$C_{16}H_{20}O_5$	13.50	903	1.6	End(100), **222(72)**, 272(41), 303(30)	292.1311	293, 275(40), 169(30)	0.03
Cyclochlorotine	$C_{24}H_{31}O_7N_5Cl_2$	8.79	800	1.4	**End**	571.1601	572, 554(8)	0.03
Cyclopaldic acid	$C_{11}H_{10}O_6$	10.46	837	2.2	End(35), **244(100)**, 274sh, 322(8)	238.0477	221, 239(17), 324	0.02
Cyclopiazonic acid	$C_{20}H_{20}O_3N_2$	20.60	1107	30	**224(100)**, 280(51)	336.1474	337	0.2
Cynodontin	$C_{15}H_{10}O_6$	28.04	1382	3	**236(100)**, 284sh, 296(18), 488sh, 516(40), 544(38), 552(39)	286.2408	ND	–
Daldinin D	$C_{21}H_{24}O_{10}$	18.11	1030	1.4	End(69), 222(sh), **304(100)**	436.1369	395, 275(61), 335(58), 437(33), 377(30)	0.2
Bis-dechlorogeodin	$C_{17}H_{14}O_7$	15.45	955	1.3	**212(100)**, 250(27), 316(14)	330.0740	299, 331(99), 287(92), 285(35)	0.02
Dechlorogriseofulvin	$C_{17}H_{18}O_6$	13.25	897	1.3	212(90), 256(60), **288(100)**, 325sh	318.1103	319, 181(95), 251(70), 341(10)	0.2
Dehydrocarolic acid	$C_9H_8O_4$	2.04	654	1.2	220sh, **252(100)**, 300(80)	180.0423	181	0.04
Dehydrocurvularin	$C_{16}H_{18}O_5$	12.48	880	1.4	End(100), **228(52)**, 288(12), 328sh	290.1154	291, 273(43), 123(29), 193(23)	0.1

Deoxybostrycin	$C_{16}H_{16}O_7$	8.90	803	1.9	**228(100)**, 304(28), 474sh, 500(30), 536(18)	320.0896	303, 321(12)	0.07
Dermoglaucin	$C_{16}H_{12}O_6$	18.60	1045	1.8	**212(100)**, 284(99), 432(40)	300.0634	301, 271(22)	0.04
Des-acetylpebrolide	$C_{22}H_{28}O_6$	12.26	876	1.2	End(100), **232(60)**, 272(4)	388.1886	308, 267(81), 389(32), 406(31), 249(3)	0.08
Desertorin A	$C_{22}H_{18}O_8$	13.19	896	1.2	**212(100)**, 236sh, 294sh, 308(50)	410.1002	411, 452(10), 821	0.1
Desertorin B	$C_{23}H_{20}O_8$	16.51	984	1.4	**208(100)**, 236sh, 294sh, 308(50)	424.1158	425, 849	0.2
Desertorin C	$C_{24}H_{22}O_8$	18.40	1039	1.4	**212(100)**, 236sh, 294sh, 308(60)	438.1315	439, 480(20), 877	0.2
Des-methoxyviridiol	$C_{19}H_{16}O_5$	9.17	809	1.4	232(40), **280(100)**, 320(12), 332(11), 402(18)	324.0998	325, 343(69), 366(10)	0.01
Desmosterol	$C_{27}H_{44}O$	45.62	2156	3.0	**End**	384.3392	367, 426(45)	0.05
Dethiosecoemestrin	$C_{27}H_{20}N_2O_{10}$	30.65	1495	1.6	End(100), **224(91)**, 284(14)	532.1118	130, 404(30), 406(25), 388(15), 533(10)	0.008
Diaporthin	$C_{13}H_{14}O_5$	12.38	878	1.3	**244(100)**, 276(13), 286sh, 328(13)	250.0841	233, 251(85), 205(35), 191(25), 177(10)	0.07
Diaportin acid	$C_{13}H_{13}O_7$	8.81	801	3	**244(100)**, 276(13), 286sh, 328(13)	281.0661	281, 235(78)	0.03
Diaportinol	$C_{13}H_{14}O_6$	8.64	797	1.4	**244(100)**, 276(12), 286sh, 328(12)	266.0790	267, 249(65), 219(20), 231(18), 281(12)	0.02
Dichlorodiaportin	$C_{13}H_{12}O_5Cl_2$	17.23	1004	1.3	**244(100)**, 276(12), 286sh, 328(12)	318.0062	319, 260(5), 205(5)	0.03
cis-Dihydrofusarubin	$C_{15}H_{16}O_7$	8.02	784	1.3	208(65), **244(100)**, 276(36), 300(24), 388(44)	308.0896	279, 291(62), 221(38), 261(35), 372(27), 364(25)	0.06
trans-Dihydrofusarubin	$C_{15}H_{16}O_7$	9.25	810	1.3	208(65), **244(100)**, 276(36), 300(24), 388(44)	308.2878	279, 291(62), 261(30), 309(20), 372(40)	0.07
Dihydrojasmonic acid	$C_{12}H_{20}O_3$	12.59	883	1.5	**End(100)**, 210sh(10), 288(19)	212.1412	254, 195(95), 194(90), 135(100), 213(18)	0.05
2′,3′-Dihydrosorbicillin	$C_{14}H_{18}O_3$	22.51	1172	1.4	216(100), 232sh, 284(80), 328(30)	234.1256	235, 165(88)	0.1
Dihydroxyaflavinine	$C_{28}H_{39}NO_3$	17.20	1003	1.4	End(91), **224(100)**, 284(19)	437.2930	420, 402 (40), 438(22)	0.03
3,5-Dimethyl-6-hydroxyphthalide	$C_{11}H_{12}O_3$	13.80	911	1.4	**208(100)**, 240(65), 300(30)	192.0786	193, 234(8)	0.07
Dimethylphthalate	$C_{10}H_{10}O_4$	11.00	848	1.3	**End(100)**, 228(22), 276(5)	194.0579	163	0.05
Dipicolinic acid	$C_7H_5NO_4$	1.25	637	1.4	**End(100)**, 220sh, 272(40)	167.0219	168, 140(20)	0.02
Dithiosilvatin	$C_{18}H_{22}O_3N_2S_2$	21.01	1121	1.3	**End(100)**, 228(38), 272(22)	378.1072	311, 379(60), 279(60), 251(50)	0.05
Duclauxin	$C_{29}H_{22}O_{11}$	20.36	1099	1.3	204(64), **228(100)**, 264sh, 320(13), 340sh	546.1162	515, 547(20), 588(8)	0.06
Dustanin	$C_{30}H_{52}O_2$	42.25	2007	1.6	**End**	444.3967	409, 427(10)	8
Echinulin	$C_{29}H_{39}O_2N_3$	26.53	1323	1.5	End(98), **232(100)**, 280(24)	461.3042	462, 406(80), 338(30), 394(25)	0.2
Emestrin	$C_{27}H_{22}N_2O_{10}S_2$	16.05	972	1.5	**End(100)**, 230sh, 260sh, 282sh	598.0716	517, 499(55), 535(20), 489(20), 599(10)	0.01
Emestrin B	$C_{27}H_{22}N_2O_{10}S_3$	15.50	998	1.4	End, 218sh(68), **255(38)**, 284sh	630.0437	517, 499(21), 613(2), 631(10)	0.01
Emindole DA	$C_{28}H_{39}NO$	30.64	1494	1.6	End(100), **224(96)**, 284(18), 290sh	405.3032	130, 406(48), 388(30), 438(20)	0.02
Emindole DB	$C_{28}H_{39}NO_2$	30.54	1490	1.7	End(100), **224(96)**, 284(18), 290sh	421.2981	130, 422(52), 404(45), 454(18)	0.02
Emodin	$C_{15}H_{10}O_5$	20.14	1092	1.5	**222(100)**, 258sh, 268(55), 288(64), 440(38)	270.0528	271, 312(20)	0.01
Epicorazine A	$C_{18}H_{16}N_2O_6S_2$	7.20	766	0.9	**End(100)**, 228sh(50)	420.0450	421, 485(10)	0.4
Epi-dechlorogriseofulvin	$C_{17}H_{18}O_6$	12.86	889	1.3	212(90), 256(70), **288(100)**, 325sh	318.1103	319, 181(95), 251(70), 341(10)	0.4
Epoxysuccinic acid	$C_4H_4O_5$	31.97	1553	3[j]	**End**	132.0059	335, 221(91), 177(91), 133(90)	13
Equisetin	$C_{22}H_{31}NO_4$	28.12	1385	3.9	End(100), 236(38), **296(63)**	373.2253	374, 175(40), 365(30)	0.07
Ergosterol	$C_{28}H_{44}O$	47.50	2239	1.6	End(100), **272(100)**, 284(100), 290sh	396.3392	377, 295(18), 253(8)	0.03
Erythroglaucin	$C_{16}H_{12}O_6$	27.66	1439	2	230(100), 256(52), **276(53)**, 304(41), 370sh, 492(42), 518sh	300.0634	301, 342(20)	0.006
Ethisolide	$C_9H_{10}O_4$	4.72	712	1.9	**206**	182.0579	137, 169(55), 215(45), 165(30), 224(22), 183(18)	0.02
Expansolide	$C_{17}H_{22}O_5$	16.50	984	10	**End**	306.1467	307, 306(79)	1
Ferulic acid	$C_{10}H_{10}O_4$	4.00	697	1.9	216(69), 236(62), 298sh, **322(100)**	194.0579	177, 186(11), 195(10), 236(5)	0.04
Flavoglaucin	$C_{19}H_{28}O_3$	31.35	1526	1.6	**End(100)**, 240(36), 276(36), 388(16)	304.2038	249, 305(40)	0.07
Formyl-xanthocillin X	$C_{18}H_{16}N_2O_4$	4.00	697	1.2	End(70), 220(30, 278sh, **338(100)**	324.1110	280, 297(48), 191(42), 347(28), 347(23)	0.02
Frequentin	$C_{14}H_{20}O_4$	15.00	943	1.4	**232**	252.3104	ND	–
Fructigenine A	$C_{27}H_{31}O_3N_3$	19.59	1076	1.3	**204(100)**, 248(28), 282sh	445.2365	446, 376(8), 487(6)	0.04
Fucosterol	$C_{29}H_{48}O$	49.13	2311	1.9	**End**	412.3705	454, 395(72), 428(26), 297(12)	0.008

Table 1. Continued

Metabolite	Formula	Retention time (min)	Retention index	Peak symmetry[a]	UV absorption (nm) in % of UV-max	Mono isotopic mass	Predominant mono isotopic ions in % of base peak	Relative sensitivity factor[b]
Fulvic acid	$C_{14}H_{12}O_8$	11.76	894	4.0	212(100), 232(70), 340sh(50), **384(81)**	308.0532	291, 273(70)	0.3
Fumagillin	$C_{26}H_{34}O_7$	23.26	1197	1.3	End(85), **232(100)**	458.2305	509	0.6
Fumagillol	$C_{16}H_{26}O_4$	7.85	780	1.4	**End**	282.1831	283, 251(62), 233(42), 265(32), 323(26)	0.05
Fumiguinazoline F	$C_{21}H_{18}N_4O_2$	14.90	941	1.3	**220(100)**, 272(22),305sh, 216sh	358.1430	357, 340(20), 398(20)	0.1
Fusaproliferin	$C_{27}H_{40}O_5$	22.50	1171	1.4	End(100), **264(58)**	444.2876	385, 403(30), 466(30), 367(30)	1
Fusaric acid	$C_{10}H_{13}NO_2$	3.56	687	11	End(100), 228(32), **272(45)**	179.0946	180, 152(85)	0.05
Fusarin C	$C_{23}H_{29}NO_7$	17.45	1010	1.4	258sh, **366(100)**	431.1944	454, 436(30), 495(29), 364(25)	0.02
Fusarochromanone	$C_{15}H_{20}N_2O_4$	10.80	844	12	212(80), **252(100)**, 280(41), 388(56)	292.1423	293, 275(78), 234(45), 192(25)	0.2
Fusarubin	$C_{15}H_{14}O_7$	11.71	864	3	**228(100)**, 304(30), 474sh, 500(28), 526sh	306.0740	289, 247(90), 307(15)	0.02
Fusicoccin	$C_{36}H_{56}O_{12}$	18.44	1041	1.2	**204**	680.3772	313, 703(92), 373(70), 281(60), 681(15)	0.1
Fusidic acid	$C_{31}H_{48}O_6$	24.55	1247	1.6	**End(100)**, 220sh(65)	516.3451	457, 534(20), 439(18), 421(17)	0.2
Fusoxysporone	$C_{20}H_{30}O$	32.32	1569	1.5	End(100), **244(85)**	286.2297	287, 269(22), 175(19), 328(12)	0.4
Gallic acid	$C_7H_6O_5$	1.30	638	1.8	**212(100)**, 272(60)	170.0215	127, 212(95), 171(85), 153(60)	0.0003
Gentisylalcohol	$C_7H_8O_3$	1.30	638	1.3	End(100), 218sh(65), **292(51)**	140.1387	123, 164(95), 245(30)	0.008
Gibberellic acid	$C_{19}H_{22}O_6$	3.80	692	1.4	**End**	346.1416	283, 311(65), 329(55), 239(45), 265(40)	0.02
Gibepyrone A	$C_{10}H_{12}O_2$	13.81	911	1.3	End(89), 236(100), **332(92)**	164.0837	165, 206(15)	0.1
Gibepyrone F	$C_8H_8O_3$	2.80	671	1.4	208(92), 248(18), **308(100)**	152.0473	153, 194(60)	0.1
Gliotoxin	$C_{13}H_{14}O_4N_2S_2$	10.05	828	1.3	**End(100)**, 268(34)	326.0395	263, 245(45), 227(15)	0.06
Gliovirin	$C_{20}H_{20}N_2O_8S_2$	12.31	877	1.6	End(100), 244(40), **344(80)**	480.0661	481, 463(10)	0.04
Griseofulvin	$C_{17}H_{17}O_6Cl$	15.38	953	1.3	212(98), 237(88), 251sh, **292(100)**, 325(24)	352.1000	353, 285(12), 165(12), 215(10)	0.05
Griseophenone C	$C_{16}H_{16}O_6$	13.54	904	1.4	**205(100)**, 227sh(44), 297(50), 337sh(12)	304.0947	165, 305(90), 185(12), 139(10)	0.008
Helminthosporin	$C_{15}H_{10}O_5$	26.14	1308	1.7	**231(100)**, 255(49), 288(23), 484(30), 518sh	270.0528	271	0.0004
Helvolic acid	$C_{33}H_{44}O_8$	23.30	1198	1.6	End(93), **232(100)**	568.3036	509, 586(18), 632(8)	0.3
Histamin	$C_5H_9N_3$	1.60	645	9	**212**	111.0796	112	0.05
5′-Hydroxyasperentin	$C_{16}H_{20}O_6$	8.46	793	1.4	**214(100)**, 267(68), 300(28)	308.1260	309, 209(48), 291(30), 173(25)	0.04
p-Hydroxybenzoic acid	$C_7H_6O_3$	1.91	652	1.5	End(100), 208sh(85), **255(92)**	138.0317	180, 121(65), 139(50)	0.001
p-Hydroxycinnamic acid	$C_9H_8O_3$	3.30	682	1.4	213(43), 227(51), 293sh, **308(100)**	164.0473	147, 165(6), 206(5)	0.02
5-Hydroxymaltol	$C_6H_6O_4$	1.69	647	8	End(100), 216sh(65), 262sh, **287(72)**	142.0266	143, 184(6)	0.05
4-Hydroxymellein	$C_{10}H_{10}O_4$	6.20	744	1.5	**208(100)**, 244(21), 312(16)	194.0579	177, 195(50), 149(50)	0.02
ω-Hydroxypachybasin	$C_{15}H_{10}O_4$	14.87	940	1.3	End(85), 222(61), **258(100)**, 277sh(45), 334(10), 440(20)	254.0579	255, 278(12), 296(15)	0.04
p-Hydroxyphenylacetic acid	$C_7H_6O_3$	2.01	654	1.8	End(100), **224(43)**, 276(9)	138.0317	107, 148(20)	0.0006
Indolacetic acid	$C_{12}H_{13}NO_3$	7.10	764	1.4	**220(100)**, 278(19), 286sh	219.0895	130, 167(30), 171(15),	0.005
Insulicolide A	$C_{22}H_{25}NO_8$	14.40	927	1.3	End(100), 212sh(75), **260(65)**	431.1580	247, 288(65), 414(37), 265(28), 306(27)	0.005
Insulicolide B	$C_{22}H_{25}NO_8$	12.59	883	1.4	End(100), 210sh(78), **262(60)**	431.1580	414, 288(38), 247(32), 217(28), 432(17)	0.05
Iodinine	$C_{12}H_8N_2O_4$	14.64	934	4	**288(100)**, 344(8), 524(8)	244.0484	228, 245(38)	0.005
Islandicin	$C_{15}H_{10}O_5$	27.88	1376	8	**230(100)**, 252(69), 292(23), 264sh, 492(35)	270.0528	ND	–
Isoemodin	$C_{15}H_{10}O_5$	15.12	947	1.4	End(55), **224(100)**, 256(64), 286sh, 432(30)	270.0528	271, 312(30), 294(18)	0.003
Isomarticin	$C_{18}H_{16}O_9$	12.33	877	1.5	**228(100)**, 304(30), 472sh, 500(27), 532sh	376.0794	377, 359(12), 303(10)	0.02
Italicic acid	$C_{15}H_{16}O_6$	12.70	885	0.9	240(52), 268(48), **336(100)**	292.0947	275, 293(62), 247(48), 310(25)	0.2

Italicic acid-methyl ester	$C_{16}H_{18}O_6$	17.70	1018	0.9	240(50), 272(45), **336(100)**	306.1103	275, 247(42), 307(32)	0.3
Italinic acid	$C_{15}H_{18}O_6$	16.13	974	1.1	228(52), 248(50), **312(100)**	294.1103	295, 277(58), 327(50), 313(25)	0.1
Jasmonic acid	$C_{12}H_{18}O_3$	11.87	867	3	**End**	210.1256	133, 151(98), 193(70), 211(50)	0.005
Jasmonic acid-methyl ester	$C_{13}H_{20}O_3$	17.43	1010	3	**End**	224.1412	225, 207(70), 255(5)	0.05
Javanicin	$C_{15}H_{14}O_6$	14.46	929	1.8	**228(100)**, 304(31), 480sh, 504(28), 538sh	290.0790	291, 249(10), 354(5)	0.1
Kojic acid	$C_6H_6O_4$	1.80	649	1.0	**216(100)**, 268(78)	142.0266	143, 184(18)	0.02
Kotanin	$C_{24}H_{22}O_8$	17.92	1025	1.4	**208(100)**, 235sh, 296sh, **308(47)**, 316sh	438.1315	439	0.4
Lactone 1 (CAS[1] 334829-27-5)	$C_{16}H_{12}O_6$	13.25	897	1.4	End(75), 232(94), **256(100)**, 298(40), 364(18)	300.0634	269, 301(30), 364(10)	0.1
Lactone 2 (CAS 334829-28-6)	$C_{16}H_{12}O_7$	9.89	824	1.4	End(60), 236(63), **264(100)**, 298(28), 388(18)	316.0583	285, 317(13)	0.03
Lambertellin	$C_{14}H_8O_5$	14.75	937	1.4	**212(100)**, 288(79), 432(21)	256.0372	298, 274(20), 320(15), 257(10)	0.004
Lanosterol	$C_{30}H_{50}O$	47.93	2258	2	**End**	426.3862	468, 439(15), 455(10)	0.02
Ascorbic acid	$C_6H_8O_6$	1.03	632	1.8	**244**	176.0321	141, 177(70), 194(40)	0.001
Leucyltryptophanyldiketopiperazine	$C_{17}H_{21}N_3O_2$	8.45	793	1.2	**220(100)**, 280(18)	299.1634	300, 130(20), 341(10), 599(10)	0.11
Lichexanthone	$C_{16}H_{14}O_5$	26.89	1337	1.4	208(71), **242(100)**, 308(65), 341sh	286.0841	287	0.3
L-Phenylalanin	$C_9H_{11}NO_2$	1.38	640	3	200(100), **210(98)**, 256(5)	165.0790	120, 166(45), 161(15), 131(15), 207(5)	0.05
L-tyrosin	$C_9H_{11}NO_3$	1.27	638	1.5	End(100), **224(45)**, 276(12)	181.0739	165, 136(95), 147(31), 182(30)	0.03
Luteoskyrin	$C_{30}H_{22}O_{12}$	22.50	1171	7	264(20), 270sh, 300(18), **344(100)**	574.1111	456, 438(48), 420(17), 478(10)	0.8
Macrosporin	$C_{16}H_{12}O_5$	19.65	1077	1.6	224(53), **284(100)**, 309sh, 280(20)	284.0685	285, 326(10)	0.008
Maculosin	$C_{14}H_{16}N_2O_3$	1.58	644	1.4	**End(100)**, 220sh(30), 275(5)	260.1161	261, 302(20), 136(12)	0.01
Marticin	$C_{18}H_{16}O_9$	13.48	902	1.6	**228(100)**, 304(33), 480sh, 500(29), 532sh	376.0794	377, 359(10), 303(10), 221(8)	0.04
3-Methoxyviridicatin	$C_{16}H_{13}NO_2$	15.52	957	1.4	294(96), **226(100)**, 280(20), 315sh, 324(22), 334sh	251.0946	252	0.6
6-Methylsalicylic acid	$C_8H_8O_3$	8.19	787	0.4	**208(100)**, 244(21), 304(10)	152.0473	135, 399(45), 194(20), 153(15)	0.005
Mevinolin	$C_{24}H_{36}O_5$	24.75	1254	1.6	**238(100)**, 246sh(70)	404.2563	285, 199(60), 405(60), 303(40), 243(35), 427(30)	0.09
Mitomycin C[h]	$C_{15}H_{18}N_4O_5$	2.57	666	1	216(100), 242sh, **360(100)**	334.1277	242, 357(21), 274(14), 335(12), 398(11)	0.5
Mitorubrin	$C_{21}H_{18}O_7$	18.60	1045	1.3	216(88), **268(100)**, 294sh, 350(88), 361sh	382.1053	233, 215(60), 151(50), 383(10)	0.01
Mitorubrinic acid	$C_{21}H_{16}O_9$	12.86	889	1.4	212(78), **272(100)**, 296sh, 448(65), 362sh, 393sh, 418sh, 448sh	412.0794	151, 413(8), 245(7), 262(6)	0.01
Mitorubrinol	$C_{21}H_{18}O_8$	12.44	879	1.3	212(94), **268(100)**, 294sh, 352(88), 363sh	398.1002	249, 151(65), 231(40), 399(15)	0.007
Mitorubrinol acetate	$C_{23}H_{20}O_9$	16.79	991	1.4	216(90), **266(100)**, 294sh, 348(88)	440.1107	291, 151(45), 441(25), 273(20)	0.001
Mizoribine	$C_9H_{13}N_3O_6$	0.95	184	3	End(82), 244(65), **280(100)**	259.0804	128, 169(80), 260(70)	0.01
Mollisin	$C_{14}H_{10}Cl_2O_4$	21.35	1132	1.3	**208(100)**, 260(75), 420(11)	311.9956	313, 277(50), 354(10)	0.0003
Moniliformin	$C_4H_2O_3$	0.82	628	1.3	**228(100)**, 260(31)	98.0004	ND	–
Monorden	$C_{18}H_{17}ClO_6$	12.82	888	1.4	**204(100)**, 276(46)	364.0714	347, 277(82), 321(50), 365(40), 303(40)	0.002
Mycophenolic acid	$C_{17}H_{20}O_6$	15.14	947	1.5	**216(100)**, 252(24), 304(12)	320.1260	321, 343(22), 297(18), 303(15)	0.05
Myriocin	$C_{21}H_{39}NO_6$	20.07	1028	5	**End**	401.2777	402, 384(14), 424(10)	1
Nectriafurone	$C_{15}H_{12}O_7$	13.48	902	5.4	End(100), **240(81)**, 258(80), 324(25), 356sh, 444(57), 464sh	304.0583	287, 259(10), 244(5)	0.09
Nidulin	$C_{20}H_{17}Cl_3O_5$	25.03	1265	1.6	204(100), 223sh(90), 268(18)	442.0142	291, 443(60), 151(52)	0.007
Nigragillin	$C_{13}H_{22}ON_2$	6.53	752	9	**268**	222.1732	223, 129(58)	0.2
3-Nitropropionic acid	$C_3H_5O_4N$	1.50	643	1.6	**204**	119.0219	257, 271(45)	0.0005
Nominine	$C_{28}H_{39}NO$	32.80	1590	1.6	End(100), **224(94)**, 284(18), 291sh	405.3032	388, 406(60), 447(12)	0.04
Norjavanicin	$C_{14}H_{12}O_6$	11.78	865	4	212sh(72), **224(100)**, 298(37), 485sh(29), 498(30), 535sh	276.0634	277, 235(32), 318(18)	0.3
Norlichexanthone	$C_{14}H_{10}O_5$	14.90	941	2	204(65), **242(100)**, 267sh, 312(60), 346sh	258.0528	259	0.03
Nortryptoquivaline	$C_{28}H_{28}N_4O_7$	21.02	1121	1.5	**208(100)**, 228(90), 255sh, 274sh, 308(8), 318sh	532.1958	533, 516(70), 471(30), 261(15)	0.2
Oleic acid	$C_{18}H_{34}O_2$	36.47	1752	1.4	**End**	282.2559	265, 247(90), 135(90), 121(80), 149(70), 163(40)	0.0006
Oosporein	$C_{14}H_{10}O_8$	1.70	647	1.5	End(92), **288(100)**	306.0376	174, 307(50), 289(40)	0.0001

Table 1. Continued

Metabolite	Formula	Retention time (min)	Retention index	Peak symmetry[a]	UV absorption (nm) in % of UV-max	Mono isotopic mass	Predominant mono isotopic ions in % of base peak	Relative sensitivity factor[b]
Ophiobolin G	$C_{25}H_{34}O_2$	30.05	1468	1.4	**236**	366.2559	367, 349(41), 733(90), 430(18), 307(12)	0.2
Orsellinic acid	$C_8H_8O_4$	3.51	686	0.8	**212(100)**, 260(44), 296(17)	168.0423	151	0.005
Oxalic acid	$C_2H_2O_4$	1.80	649	1.4	**End(100)**, 248(4)	89.9953	ND	–
Pachybasic acid	$C_{15}H_8O_5$	15.70	962	1.2	208(82), 224(80), **258(100)**, 278sh, 340(10), 404(20)	268.0372	310, 269(50), 550(50), 533(35), 631(20)	0.001
Pachybasin	$C_{15}H_{10}O_3$	23.70	1214	1.4	End(94), 224(61), 248sh, **260(100)**, 277sh(47), 332(10), 404(20)	238.0630	239, 280(30)	0.001
Palitantin	$C_{14}H_{22}O_4$	12.50	881	1.4	**232**	254.1518	237, 219(82), 255(62), 201(55), 173(45)	0.002
Paracelsin		13.80	911	1.3	End(100), 218sh(56), **284(70)**	414	415, 320(13), 199(7)	0.1
Paspaline	$C_{28}H_{39}NO_2$	32.62	1582	1.6	207sh(48), **232(100)**, 280(29)	421.2981	130, 404(70), 422(69), 454(12)	0.08
Paspalinin	$C_{27}H_{31}NO_4$	25.25	1274	1.7	End(60), **232(100)**, 273(27)	433.2253	434, 376(98), 130(55)	0.04
Patulin	$C_7H_6O_4$	1.49	642	1.4	**276**	154.0266	213, 109, 155, 169	0.0003
Penicillic acid	$C_8H_{10}O_4$	3.63	689	1.4	End(48), **228(100)**	170.0579	125, 153(90), 171(40)	0.04
Penicillin G	$C_{16}H_{18}O_4N_2S$	10.57	839	0.9	**End(100)**, 206sh(75)	334.0987	367, 160(25), 335(20), 389(10)	0.5
Phaseic acid	$C_{15}H_{20}O_5$	8.13	786	1.2	**264**	280.1311	165, 263(28), 123(12)	0.03
Phoenicin	$C_{14}H_{10}O_6$	2.20	658	0.4	End(78), 213sh(66), **268(100)**, 432broad(4)	274.0477	275, 247(22), 219(21), 257(16), 338(15)	0.02
Phomarin	$C_{15}H_{10}O_4$	19.08	1060	1.5	220(90), **268(100)**, 294sh, 415(21)	254.2420	255, 296(10)	0.01
Physcion	$C_{16}H_{12}O_5$	26.20	1311	6.4	End(60), **224(100)**, 257sh, 268(54),288(55), 436(36)	284.2683	285, 326(10)	0.03
PI-3	$C_{14}H_{12}O_8$	2.13	656	1.6	**220(100)**, 256sh, 296(30), 326(40)	308.0532	291, 273(90), 231(18), 249(60)	0.007
PR-1635	$C_{18}H_{15}N_2O_5$	7.30	768	0.8	End(85), 246(35), **362(100)**	339.0981	339, 311(63), 677(25)	0.008
Preechinulin	$C_{19}H_{23}O_2N_3$	11.32	855	1.3	End(79), **224(100)**, 284(20)	325.1790	258, 326(45), 198(45), 270(40), 130(30)	0.07
PR-imine	$C_{17}H_{21}NO_5$	11.05	849	8	**252(100)**, 287sh(38)	319.1420	320	0.8
Propyl-3,4,5-trihydroxybenzoate	$C_{10}H_{12}O_5$	7.58	774	1.3	**216(100)**, 272(48)	212.0685	212, 171(65), 127(40), 153(30)	0.01
PR Toxin	$C_{17}H_{20}O_6$	14.20	922	0.16	**256**	320.1260	321, 279(15), 384(10)	0.6
Puberuline	$C_{27}H_{29}N_3O_3$	18.40	1039	1.2	**204(100)**, 248(30), 280sh	443.2209	444, 376(52), 485(19)	0.00003
Puberulonic acid	$C_9H_4O_7$	1.32	639	1.3	End(60), **276(100)**, 318(49), 363sh, 376(32), 412(30)	223.9957	225	0.008
Purpurin	$C_{14}H_8O_5$	17.06	999	1.1	204(72), **256(100)**, 296(30), 456sh, 480(28), 508sh	256.0372	257, 298(30)	0.01
Purpurogenone	$C_{29}H_{20}O_{11}$	21.56	1140	1.3	**220(100)**, 252(80), 273sh(50), 305(32), 364sh, 380(29), 490sh, 496sh, 520(27), 556sh	544.1006	545	0.03
Pyrogallol	$C_6H_6O_3$	1.43	641	1.6	**207(100)**, 224sh(85), 264(46)	126.0317	127, 109(50), 150(28), 168(25)	0.001
2-Pyruvoylaminobenzamide	$C_{10}H_{10}O_3N_2$	1.40	640	2	**218(100)**, 245sh(28), 296(7)	206.2011	190, 148(8), 207(8), 248(7)	0.03
Questin	$C_{16}H_{12}O_5$	16.22	976	1.5	**224(100)**, 250sh, 284(64), 436(27)	284.2683	285	0.02
Questinol	$C_{16}H_{12}O_6$	9.39	813	1.4	**224(100)**, 250sh, 284(64), 436(27)	300.2677	301	0.04
Radicinin	$C_{12}H_{12}O_5$	6.70	755	0.8	208(70), 220(71), 236sh, 272(26), **344(100)**	236.0685	237, 219(25), 193(10)	0.4
Ravenelin	$C_{14}H_{10}O_5$	19.02	1058	1.4	End(75), 236sh(60), **260(100)**, 340(37), 398(10)	258.0528	257, 259(60), 320(40)	0.01
Riboflavin	$C_{17}H_{20}N_4O_6$	1.65	646	1.3	224(91), **268(100)**, 371(30), 448(41)	376.1383	377, 399(4)	0.1
Rosenonolactone	$C_{20}H_{28}O_3$	21.35	1132	1.8	**End(100)**, 214sh(10), 288(3)	316.2038	317, 253(55), 271(40), 299(30)	0.1
Roseopurpurin	$C_{16}H_{12}O_6$	9.32	812	1.7	End(74), **220(100)**, 248(54), 284(67), 436(28)	300.0634	301	0.04
Rubratoxin A	$C_{26}H_{32}O_{11}$	12.09	872	1.6[m]	**204(100)**, 254sh(15)	520.1945	521, 485(72), 389(60), 538(43), 503(41)	0.1
Rubratoxin B	$C_{26}H_{30}O_{11}$	16.70	989	1.6	**204(100)**, 252(32)	518.5176	519, 536(82), 560(25), 501(24), 582(12), 483(10)	0.3
Rugulosin	$C_{30}H_{22}O_{10}$	19.74	1080	1.6	End(88), 252(100), 274sh, **391(100)**	542.1213	543, 273(12)	0.02
Salicin	$C_{13}H_{18}O_7$	1.32	639	1.4	**End(100)**, 211(sh), 268(15)	286.1053	107, 213(32), 148(30), 304(12), 309(11	0.01
Salicyclic acid	$HOC_6H_4CO_2H$	5.50	729	0.5	**204(100)**, 232(22), 300(12)	138.0317	121, 251(90), 371(70)	0.005
Sclerotigenin	$C_{16}H_{11}N_3O_2$	7.25	767	1.7	215sh(78), **230(100)**, 267(22), 280(20), 310(10), 319sh	277.0851	278, 319(10), 341(5)	0.07

Scytalidine	$C_{22}H_{28}O_7$	25.96	1301	1.4	**204(100)**, 252(54)	404.1835	422, 387(30), 369(26), 462(22), 405(18)	0.004
Scytalone	$C_{10}H_{10}O_4$	2.40	662	1.9	216(98), 230sh(78), **284(100)**, 316sh(45)	194.0579	195, 177(25), 149(10)	0.02
Secalonic acid D	$C_{32}H_{30}O_{14}$	21.01	1121	2.3	End(82), 216(62), 237(48), 264(40), **337(100)**, 383sh	638.1636	639	0.8
Shikimic acid	$C_7H_{10}O_5$	2.00	654	4	**210**	174.0528	260, 166(93), 300(70)*	0.2
Skyrin	$C_{30}H_{18}O_{10}$	24.96	1263	2.9	**224(100)**, 256(81), 296(52), 456(40)	538.0900	539, 521(12)	0.007
SMTP-6	$C_{34}H_{40}N_2O_6$	24.33	1238	1.7	**216(100)**, 260(20), 284sh,292sh,206sh	572.2886	573	0.1
SMTP-7	$C_{51}H_{68}N_2O_{10}$	28.32	1393	1.7	**216(100)**, 260(22), 304(8)	868.4874	869	0.1
SMTP-8	$C_{52}H_{70}N_2O_{10}$	30.93	1507	1.7	**216(100)**, 256(20), 302(8)	882.5030	883	0.2
Solaniol	$C_{15}H_{16}O_6$	13.80	911	1.8	End(60), **228(100)**, 308(30), 480sh, 504(28), 542sh	292.0947	275, 257(15), 338(8)	0.03
Soranjidiol	$C_{15}H_{10}O_4$	19.93	1086	1.6	220(90), **268(100)**, 293sh(50), 412(26)	254.0579	255, 296(17)	0.005
Sorbicillin	$C_{14}H_{16}O_3$	21.46	1136	1.3	204(100), **324broad(83)**	232.1099	233, 216(16)	0.1
Spinulosin	$C_8H_8O_5$	2.35	661	1.4	200(81), 212(60), **296(100)**	184.0372	185, 367(95), 463 (45)	0.002
Staplabin	$C_{28}H_{39}NO_6$	22.07	1157	1.5	**216(100)**, 256(21), 302(6)	485.2777	468	0.1
Steckiin	$C_{22}H_{26}O_9$	7.95	782	1.1	**212(100)**, 236(64), 284(78), 308sh(45)	434.1577	435, 417(88), 452(25), 476(10)	0.1
Stemphone	$C_{30}H_{42}O_8$	22.80	1181	1.8	End(100), **268(50)**, 296(5)	530.2880	471, 453(95), 387(92), 429(85), 513(70), 531(60)	0.065
Stipitatic acid	$C_8H_6O_5$	1.36	640	1.8	**266(100)**, 310sh, 360(20), 415sh	182.0215	183, 459(90), 224(45)	0.004
Sulochrin	$C_{17}H_{16}O_7$	13.08	893	1	**208(100)**, 216(85), 284(40), 320sh	332.0896	209, 333(9), 301(8), 396(8)	0.1
Taxol	$C_{47}H_{51}NO_{14}$	20.34	1098	1.4	**End(100)**, 228(40)	853.3310	854, 286(47), 509(38), 569(34), 569(35)	0.1
Tentoxin	$C_{22}H_{30}N_4O_4$	13.80	911	1.5	End(100), 218(55), **280(78)**	414.2267	415, 437(28), 302(10), 199(7)	0.4
Tenuazonic acid	$C_{10}H_{15}O_3N$	11.82	866	0.08	End(69), 222(60), **284(100)**	197.1052	456, 198(52), 458(45)	0.1
Terrein	$C_8H_{10}O_3$	1.52	643	1.3	**282**	154.0630	137, 155(60)	0.006
Terrestric acid	$C_{11}H_{14}O_4$	4.13	700	0.6[m]	208(52), 231(22), **274(100)**	210.0892	211, 212(12), 159(11)	0.2
Terretonin	$C_{26}H_{32}O_9$	17.21	1003	1.7	End(78), **280(100)**	488.2046	489, 506(70), 471(65)	0.3
Thiamin, hydrochloride	$C_{11}H_{16}N_4OS$	2.07	655	9	200, **248(75)**, 257sh	252.1045	254	0.1
Toluhydroquinone	$C_7H_8O_2$	1.82	650	1.2[m]	**End(100)**, 217sh(22), 288(13)	124.0524	114, 155(60), 125(15), 328(15), 364(10)	0.02
Tomatine[h]	$C_{50}H_{83}NO_{21}$	15.34	952	1.7	**End(100)**, sh216(45)	1033.5458	578, 1034(63), 416(26)	30
Torreyol	$C_{15}H_{26}O$	25.46	1282	1.7	**End**	222.1984	205, 121(88), 149(40)	0.09
3,4,5-Trihydroxy-7-methoxy-2-methylanthraquinone	$C_{16}H_{12}O_6$	20.45	1102	1.6	End(70), 230(69), 260sh, **282(100)**, 313(43), 432(40)	300.0634	301, 302(20), 342(5)	0.02
Trisdechlorononornidulin	$C_{19}H_{18}O_5$	18.06	1029	1.4	**204(100)**, 254sh(30)	326.1154	327, 368(12), 271(5)	0.08
Trypacidin	$C_{18}H_{16}O_7$	15.30	951	1.4	**208(100)**, 288(55), 328sh	344.0896	239, 165(55), 345(50), 377(30)	0.08
Tryptophan	$C_{11}H_{12}N_2O_2$	1.76	648	6	**220(100)**, 280(15), 287sh	204.0899	188, 146(20), 205(10), 159(5)	0.05
Tryprostatin B	$C_{21}H_{25}N_3O_2$	12.86	778	1.3	**224(100)**, 280(20)	351.1947	352, 198(51), 296(40), 284(28)	1
Tyramine	$C_8H_{11}NO$	1.93	652	12	**End(100)**, 22(50), 276(10)	137.0841	121, 138(14)	0.09
Usnic acid	$C_{18}H_{16}O_7$	27.22	1350	6	**232(100)**, 280(72), 260sh	344.0896	345, 327(14)	0.08
Vermiculin	$C_{20}H_{24}O_8$	9.63	819	0.9	**224**	392.1471	197, 410(38), 393(28)	0.2
Verrucine A	$C_{21}H_{20}O_3N_4$	9.74	821	1.1	End(100), **230(79)**, 276(25), 308(10), 316sh	376.1535	377, 360(82)	0.1
Verrucine B	$C_{21}H_{20}O_3N_4$	12.48	880	1.4	208(100), **228(78)**, 268(28), 336(39)	376.1535	377, 360(60)	0.8
Verrucofortine	$C_{24}H_{31}N_3O_3$	17.78	1020	1.2	**208(100)**, 230(75), 264(30), 334(48)	409.2365	410, 342(18), 473(10), 432(5), 300(5)	0.4
Verrucosidin	$C_{24}H_{32}O_6$	22.38	1167	1.6	**End(100)**, 240(53), 296(34)	416.2199	153, 249(95), 197(70), 399(50), 480(50)	0.01
Verrucosine	$C_{24}H_{31}O_3N_3$	17.72	1019	1.4	**204(100)**, 248(31), 275sh	409.2365	410, 473(15), 342(10), 841(20)	0.4
Verruculogen	$C_{27}H_{33}O_7N_3$	20.20	1094	1.6	**End(100)**, 224(87), 276(16), 294(15)	511.2319	494, 352(40), 495(30)	0.1
Verruculotoxin	$C_{15}H_{20}ON_2$	6.37	748	15	**End**	511.2319	245, 217(75), 511(5)	0.5
10-Epi-verruculotoxin	$C_{15}H_{20}ON_2$	6.60	753	12	**End**	244.1576	217, 245(95)	1

Table 1. Continued

Metabolite	Formula	Retention time (min)	Retention index	Peak symmetry[a]	UV absorption (nm) in % of UV-max	Mono isotopic mass	Predominant mono isotopic ions in % of base peak	Relative sensitivity factor[b]
Vertinolide	$C_{14}H_{18}O_4$	10.90	846	1.2	232(51), **280(100)**	250.1205	251, 283(58), 201(54), 273(25)	0.1
Violaceic acid	$C_{15}H_{12}O_6$	8.80	801	1	End(100), **228(82)**, 262(68), 284sh	288.0634	271, 289(28), 330(22)	0.04
Viomellein	$C_{30}H_{24}O_{11}$	22.02	1155	1.8	228(48), **275(100)**, 360(18), 380(18), 415(17)	560.1319	561, 626(18)	0.6
Vioxanthin	$C_{30}H_{26}O_{10}$	25.24	1273	1.3	224(27), **268(100)**, 310(12), 376(23)	546.1526	423, 484(90), 467(75), 528(70), 547(30)	0.02
Viridamine	$C_{16}H_{22}N_4O_2$	11.45	858	7	End(81), 226(52), **304(100)**	302.1743	303, 344(5)	0.2
Viridicatic acid	$C_{12}H_{16}O_6$	3.00	675	3	233(88), 244(52), **265(100)**	256.0947	257, 239(80), 279(38), 123(35)	0.2
Viridicatin	$C_{15}H_{11}NO_2$	15.52	957	5	204(78), **222(100)**, 240sh(50), 288(20), 318(27)328sh	237.0790	238	0.2
Viridicatumtoxin	$C_{30}H_{31}NO_{10}$	22.80	1181	9	240(70), **284(100)**, 332(10),436(30)	565.1948	548, 549(40), 565(17), 566(14)	0.1
Viridiol	$C_{20}H_{18}O_6$	8.73	799	1.1	End(62), **253(100)**, 320(46)	354.1103	355, 396(70), 281(30), 309(18), 322(12)	0.05
Viriditoxin	$C_{34}H_{30}O_{14}$	22.78	1181	5.7	End(45), 224(40), **260(100)**, 342sh, 376(23)	662.1636	663, 647(20)	0.04
Visoltricin	$C_{13}H_{18}N_2O_2$	11.98	869	12	End(59), 236sh(32), **284(100)**	234.1368	235, 203(18)	0.5
Walleminol[e]	$C_{15}H_{24}O_2$	12.88	779	1.4	**End**	236.1776	201, 219(80)	0.001
Walleminone[e]	$C_{15}H_{24}O_3$	13.50	940	1.6	**End**	252.1725	253, 235(10)	0.001
Wortmannin	$C_{23}H_{24}O_8$	13.70	908	1.2	End(100), **260(50)**, 296(32)	428.1471	313, 295(56), 355(51), 255(30), 369(20)	0.07
Xanthocillin X	$C_{18}H_{12}O_2N_2$	17.70	1018	1.6	End(50), 240(20), **360(100)**, 380sh	288.0899	348, 371(62), 289(40), 577(30)	0.01
Xanthomegnin	$C_{30}H_{22}O_{12}$	18.64	1047	1.8	**232(100)**, 288(30), 403(20)	574.1111	575, 597(12)	0.4

[a] Peak asymmetry at 10% height.
[b] The relative sensitivity index (RSI) of the MS versus the UV (diode array data) was calculated as the peak area of the most intense ion ±0.5 u compared with peak area of the most specific and usually highest absorption trace (±2 nm) as indicated in bold.
[c] sh: Shoulder
[d] ND: Not detected.
[e] Should be analysed with an lower cone voltage.
[f] End: End absorption (<200 nm), 202±2 nm trace used for RSI calculation.
[g] Analysed with an extended mass range.
[h] Not a microfungal metabolite.
[i] dc: Double charged ion.
[j] Small acids and their derivatives may yield very strange MS spectra.
[k] Polymerisation product—also detected in crude fungal extracts.
[l] CAS: Chemical Abstracts number.
[m] Very broad peak.

needed). And similarly in last part of the run, near 100% acetonitrile, a low temperature and gas flows are needed, especially sterols suffered from poor ionisation due to high volatility and reduced surface tension of the eluent.

The most prominent and desired ion is the protonated (or quasi molecular) ion $[M+H]^+$, but other ions can be quite abundant depending on the compound, ion source parameters (cone/skimmer/fragmenter voltage), the solvents used particularly the pH, anions ions available and solvent volatility. Table 2 lists some of the most common adducts and fragments found in ESI^+ spectra from Table 1.

All cluster ions can be of diagnostic value and used to validate the identity $[M+H]^+$ ion, especially for components undergoing both fragmentation and adduct formation, but it is also important to note that cluster formation are very concentration depended [55–57]. The trichoverrols, e.g., trichoverrol A as shown in Fig. 1 show a very high affinity for dimmers $[2M+H]^+$ and $[2M+NH_4]^+$ but also show loss of water and other fragments.

Alkaloids, e.g., the roquefortines, the fumonisins and also many non-alkaloids such as the aflatoxins and territrems produce simple ESI spectra with the $[M+H]^+$ ion as the only or dominating ion.

Some small organic acids including a number of benzoic acid derivatives produced unpredictable mass spectra with a significant number of ions with

Table 2
Typical adducts, clusters and fragments seen in positive electrospray ionisation LC–MS on the components investigated

Ion structure	Mass m/z	Relative abundance
Fragments		
$[M\text{-}CO_2+H]^+$	$M_r-42.9918$	Compound dependent
$[M\text{-}2H_2O+H]^+$	$M_r-35.0133$	Compound dependent
$[M\text{-}H_2O+H]^+$	$M_r-17.0027$	Compound dependent
Clusters		
$[M+H]^+$	$M_r+1.0078$	High
$[M+Na]^+$	$M_r+22.9898$	Medium to low
$[M+NH_4]^+$	$M_r+18.0344$	Medium
$[M+CH_3CN+H]^+$	$M_r+42.0344$	Medium
$[M+CH_3CN+Na]^+$	$M_r+64.0163$	Rare
$[2M+H]^+$	$2\times M_r+1.0078$	Medium
$[2M+Na]^+$	$2\times M_r+22.9898$	Medium
$[2M+NH_4]^+$	$2\times M_r+18.0344$	Rare
$[2M+CH_3CN+H]^+$	$2\times M_r+64.0163$	Rare

Note: M_r = Molecular mono isotopic mass.

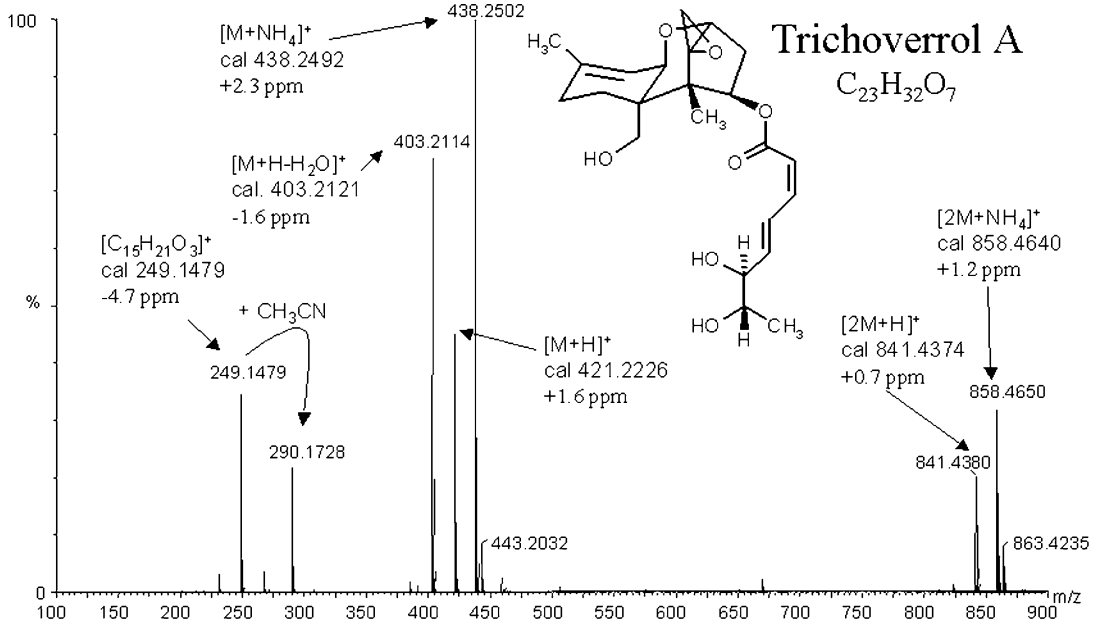

Fig. 1. ESI spectrum (6 V between the two cones) of trichoverrol A showing that the $[2M+H]^+$ here gives extra confidence on assigning the ions as $[M+H]^+$.

masses into the $[2M+H]^+$ to $[4M+H]^+$ range. This probably due to cluster formation with, e.g., water and other co-eluting compounds. Therefore, the ESI conditions used in this study are not well suited for these compounds.

The $[M+NH_4]^+$ ions were particular abundant in spectra from some of the highly oxygenated compounds. E.g., the simple and macrocyclic trichothecenes, chaetoglobosin C, the rubratoxins and many peptides (confirmed by the accurate mass determination). The simple trichothecenes with an acetyl group at C_{15} showed predominant $[M+NH_4]^+$ ions as reported by Berger et al. [58]. The abundant ammonium adducts were surprising as no ammonia was added to the mobile phases, but is most likely present in the solvents or from previous experiments [58] or formed in the source by redox processes in the electrospray. In cases of significant $[M+NH_4]^+$ adduct formation, e.g., by the trichothecenes it can be advantageous to add ammonia to the eluents to maintain a constant ammonia concentration rather than rely on the in-source production. It was observed that the $[M+NH_4]^+/[M+H]^+$ ratio of satratoxin H could vary from 20 to 70% during 1 day.

Besides adduct formation, the loss of water is common in ESI^+, hence formation of $[M+H-H_2O]^+$, $[M+H-2H_2O]^+$ ions. Some compounds, e.g., the zeralenons, the cytochalasins, asterric acid, canescin, carlosic acid, culmorin, walleminol and as well as some of the trichothecenes showed only a minor or no protonated molecular ion due to extensive loss of water and thus relative intense $[M+H-H_2O]^+$ ions which can be used as a diagnostic ion. Other ions or fragments originating from the powerful redox processes in the electrospray are sometime found, they are however very dependent on source and solvent conditions.

Reproducible mass spectra can be obtained over significant period of time if the source parameters and solvent composition are kept constant, which is a prerequisite for a (HTS) screening method. The source parameters particularly the potential difference between the two cones (skimmers, see Ref. [54] for orientation of these) do have a significant effect on the appearance of the spectra, especially for labile components. Therefore, it advised to study the effect of variation of this parameter on each instrument and optimise for minimal fragmentation, thus to favour the $[M+H]^+$ ion or other simple adduct ions. A higher total ion count can sometime be obtained by increasing the cone voltage by not necessary a higher ion current for ions of interest, as seen in Fig. 2.

Due to the lability of the trichothecenes, these has to be analysed at significantly lower cone voltages, as shown in Table 3, giving higher abundances of high mass ions others than the $[M+Na]^+$ (Fig. 2) which dominates at higher cone voltage differences. This lability of the trichothecenes have also been reported for APCI [59,60].

3.3. Accurate mass determination

Mass accuracy obtained for the metabolites in Table 1 was generally in the range of 3–4 ppm (results not shown), which corresponds to findings of others [34,35]. However, it is important keep the ion counts low to minimise the effect of dead time in the MCP detector system, (on the LCT below about 500 with 1 GHz TDC (time to digital converter) and 140 with a 3.6 GHz TDC) although software correction should work to about 1000–1500 counts [61]. Therefore mass accuracy in real LC–MS will often be highest at either the front or tail of a chromatographic peak where the ion counts is in a suitable range rather than at the peak apex where ion counts

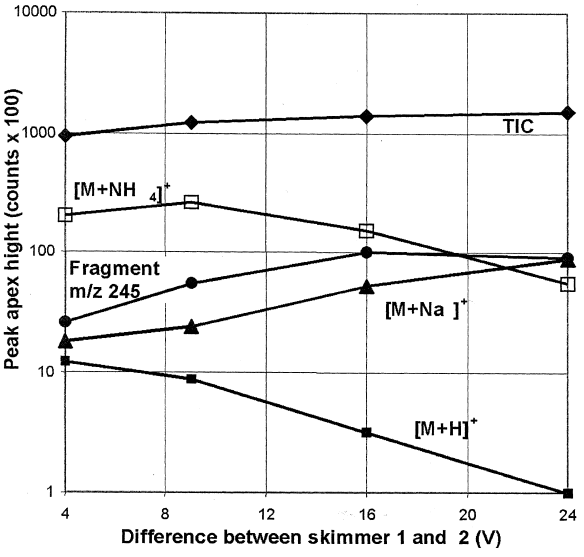

Fig. 2. Changes in ion current of neosolaniol; 6 to 24 V difference between the skimmers.

Table 3
ESI^+ spectra of various trichothecenes at a 6 V difference between cones 1 and 2

Metabolite	Mono isotopic mass	Predominant ions (m/z)	Metabolite	M_r	Predominant ions (m/z)
Nivalenol	312.1209	313, 295(71), 247(53), 265(54), 277(30)	Trichodermol	250.1569	251, 292(96), 184(12)
Deoxynivalenol	296.1260	297, 249(4)	Trichoverrol A	420.2148	438, 403(78), 421(48), 249(35), 858(32)
Fusarenone X	354.1315	355, 337(30), 247(22), 319(20), 295(18)	Trichoverrol B	420.2148	438, 443(40), 403(38), 249(25), 421(20)
Neosolaniol	382.1628	400, 305(20), 245(20), 215(18), 346(17)	Trichoverrin A	532.2672	550, 533(48), 361(38), 515(20), 555(15)
Scirpentriol	282.1467	265, 306(70), 283(50), 247(28), 217(32)	Trichoverrin B	532.2672	550, 361(46), 533(43), 515(32),555(14)
15-*O*-Acetyl-4-deoxynivalenol	338.1366	339, 321(33), 261(31), 356(18), 361(17)	Roridin A	532.2672	550, 553(20), 555(5)
Diacetoxyscirpenol	366.1679	384, 307(30), 349(29), 367(18), 755(10)	Roridin E	514.2567	532, 515(10)
HT-2 toxin	424.2097	425, 263(52), 245(38), 442(32), 215(28)	Roridin H	512.2410	513, 530(83)
Iso-T-2 toxin	466.2203	467, 484(53), 287(12), 305(7)	Isosatratoxin F	542.2152	543, 560(48), 525(24), 606(9)
T-2 Toxin	466.2203	484, 346(20), 489(20), 305(15), 215(10)	Satratoxin G	544.1945	545, 527(94), 562(50), 419(12), 249(10)
Trichodermin	292.1675	293	Satratoxin H	528.2359	529, 546(30), 511(20)

can be to high [61]. Fig. 3A–F, shows the mass accuracy across a chromatographic peak from analysis of a cultural extract, with a mass window of 3, 5, 10, 30 and 50 ppm. In this case the whole peak tail is seen within a ±2.5 ppm window, and the best precision is achieved at 500–1000 counts.

Calculating the accurate mass of multiple ions in a spectrum can be a very efficient tool to confirm a molecular composition including known adduct and fragments, but also using isotope ions, hence 2–5 ions can often be used to validate a formula as illustrated below.

In a few rare cases M^+ ions were observed, especially in spectra from several of the penitrems but also from viridicatum toxin. As such ions are uncommon in ESI they were validated using the accurate mass to show that they were not $[M+NH_4\text{-}H_2O]^+$ ions.

Finally, accurate mass are efficient to de-convolute quite complex extracts of poorly separated compounds with the same nominal mass.

3.4. Diode array detection

As seen in Table 1 UV is still a good alternative for some compounds, e.g., patulin and penicillic acid

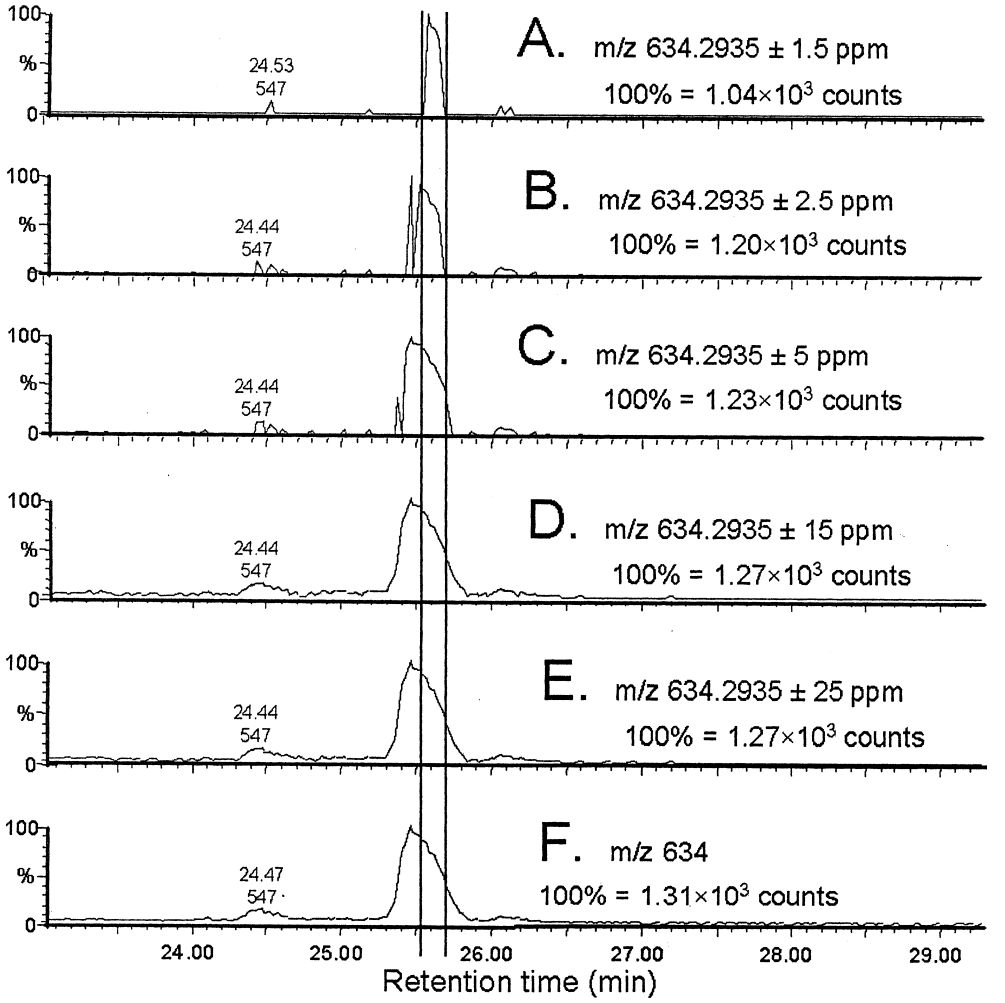

Fig. 3. Mass accuracy illustrated by plotting ion traces from protonated penitrem A with different window widths. This was from the *P. ochrochloron* extract shown in Fig. 4. The two vertical lines shows where in the peaks the precision is ±2.5 ppm from the calculated mass.

using this general screening method due to the compromise of the solvent composition that allows ESI^+-MS. Other compounds have quite unique UV spectra (fingerprints), which distinguish isomers with the same molecular formula. For unambiguous determination of many metabolites the combination of UV spectra and mass spectra were necessary, both for some less pure standards and especially for dereplication of known components not available as reference standards.

The UV sensitivity was significant reduced by formic or acetic acid normally used in positive ESI, compared to TFA. As the combination of MS and UV is crucial for dereplication of many compounds, a low concentration of TFA was chosen as modifier for the water although it does reduce the sensitivity in positive ESI-MS [62,63].

3.5. Sensitivity and detection limits

Table 4, shows the limits of detection (LOD) for some compounds (as injected on column) that was quantified. Except for the aflatoxins, the trend was that large polar compounds had lower LOD, whereas small and/or highly oxgenated molecules had high LOD. It should be noted that the instrument was tuned for high resolution and higher mass rather than sensitivity, thus the sensitivity can be improved significantly for specific components at the expense of resolution and hence mass accuracy.

Finally, in Table 1, we have included a relative sensitivity index (RSI) to illustrate the difference in response by ESI-MS and UV. Obviously it would have been more precise to determine the absolute limits of detection for each component by UV and ESI-MS, but as previously mentioned many of the standards were not totally pure and not available in quantities that could be weighed, making this impossible. The ESI responds in is highly source and solvent dependent, thus RSI may change significantly as a result of tuning, etc., and can only give an indication of the responds on other instruments, but do give an idea of the feasibility of positive ESI versus UV detection. For qualitative screening this is of less importance whereas selectivity is most important.

The RSI increase with the ESI sensitivity during the gradient to until about 90% acetonitrile (~35 min retention time or *I* 1700) due to a higher volatility of the solvents (source is optimised at about 50% acetonitrile). A general solution to these problems is to change the de-solvation parameters (temperature and gas flows) as a function of the gradient or maintain constant solvent composition by post-column modification although not very feasible [62,63]. As concentration overload in the ESI is one of the more common problems in ESI the reduced sensitivity is not a major issue.

4. Dereplication of fungal extracts

To illustrate dereplication, three plug extracts have been studied and new metabolites predicted using LC–ESI-MS–UV and the data from Table 1.

Table 4
Limits of detection for selected metabolites by LC–ESI-MS

Compound	Detection ion (m/z)	Adduct	Detection limit[a]	Compound	Detection ion (m/z)	Adduct	Detection limit[a]
Nivalenol[b]	313	$[M+H]^+$	3 ng	Isosatratoxin F[b]	543	$[M+H]^+$	400 pg
Fusarenone X[b]	355	$[M+H]^+$	700 pg	Satratoxin G[b]	545	$[M+H]^+$	1.3 ng
Deoxynivalenol[b]	297	$[M+H]^+$	600 pg	Roridin H[b]	513	$[M+H]^+$	700 pg
Neosolaniol[b]	400	$[M+NH_4]^+$	1 ng	Aflatoxin M_1	329	$[M+H]^+$	20 pg
Diacetoxyscirpenol[b]	384	$[M+NH_4]^+$	250 pg	Ochratoxin A	404	$[M+H]^+$	10 pg
HT-2 toxin[b]	425	$[M+H]^+$	800 pg	Roquefortine C	390	$[M+H]^+$	2 pg
T-2 toxin[b]	484	$[M+NH_4]^+$	125 pg	Enniatins		$[M+NH_4]^+$	1 pg
Roridin E[b]	532	$[M+NH_4]^+$	750 pg	Fumonisin		$[M+H]^+$	1–5 pg
Satratoxin H[b]	529	$[M+H]^+$	600 pg	AAL toxins		$[M+H]^+$	1–5 pg

[a] Injected on column, note that the instrument was tuned for high resolution—not high sensitivity.
[b] Analysed by a 6-V difference between the skimmers, others by a 24-V difference.

4.1. *Penicillium ochrochloron* extracts

Although the penicillia have been investigated for years, many unknown metabolites still exist within this genus and our hit rate for elucidating new compounds in *Penicillium* is still >50% [64]. *P. ochrochloron* (*P.* cf. *simplicissimum*) is known to produce two groups of compounds with interesting

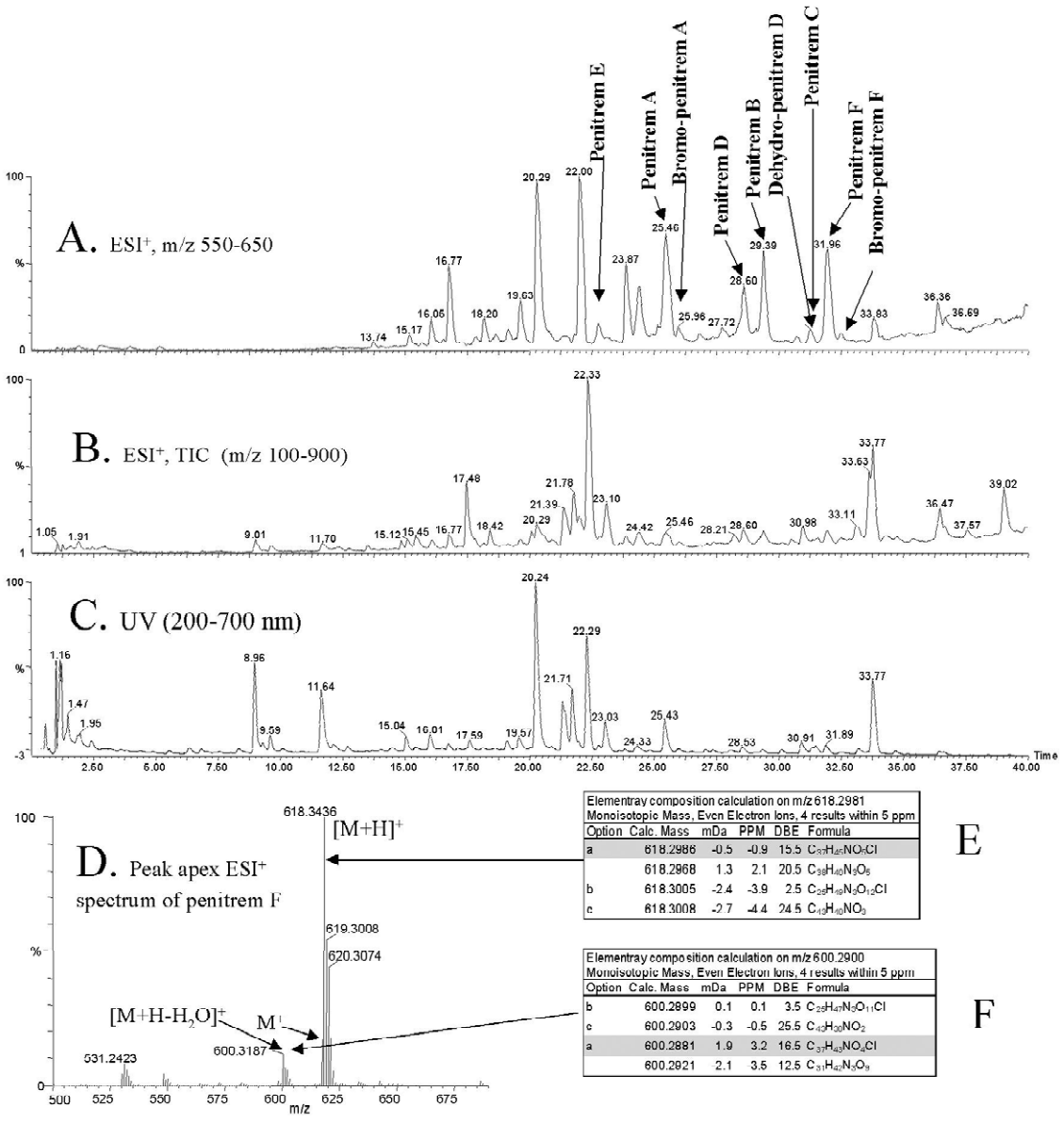

Fig. 4. *Penicillium ochrochloron*, grown for 7 days on alkaloid-forming agar [67] (0.6 cm^2 culture extracted). (A) Extracted ion chromatogram of 550 to 650 (all penitrems have molecular masses in this range); (B) total ion current chromatogram; (C) UV trace (sum of 200–700 nm). The peak apex spectrum of penitrem F is shown in D. Two of the ions ($[M+H]^+$ and $[M+H\text{-}H_2O]^+$) used for determination of penitrem F, were taken in the tail of the peak (to get an ion count <500), and are hence different than in the peak apex spectrum, the elementary composition calculations (penitrem F in grey) of them are shown in E and F, respectively.

biological activities, the okaramins [65] and the penitrems along with several other unknown metabolites. Dereplication of the penitrems B to F [66], not available as reference standards, is shown in Fig. 4, along with two undescribed analogues. The dereplication was done by combining UV spectra (identical to penitrem A), knowledge of the penitrem A fragmentation pattern, and the predicted isotope patterns. Penitrems was found to produce an M^+ ion with an intensity 25–40% of $[M+H]^+$ which together with the $[M+H\text{-}H_2O]^+$ ion (Fig. 4F) and chlorine isotope pattern (Fig. 4E and F) can be used to verify the compound by the accurate mass, as illustrated for penitrem F in Fig. 4.

For the component designated penitrem F, four formulas could be calculated within the instrument precision for the $[M+H]^+$ ion (Fig. 4E), of these three combinations matched the accurate mass of the $[M+H\text{-}H_2O]^+$ ion (Fig. 4F, a, b and c), and combining with the $[M^{37}Cl+H]^+$ ion (not shown) only two combinations (a and b in Fig. 4E–F) were possible. However, all chlorinated penitrems were followed by a small bromiated penitrem eluting 0.4–0.5 min later, which was also the case for this component, but on the bromiated analogue similar accurate mass calculations (not shown) identified this peak as bromopenitrem F, hence the preceding peak is most likely penitrem F [67].

The two peaks identified as bromopenitrem F and dehydropenitrem E were not found in CAS by the SciFinder software.

4.2. Penicillium crateriforme (P. rubrum) and instability of rubratoxins

Analysing extracts of *P. crateriforme* (*P. rubrum*), two major peaks and 3–4 minor peaks elutes between 10 and 17 min. As these peaks are also present in rubratoxin B standards (from Roth, Supelco, and also in an authentic sample from Dr. M. Moss), this chromatographic peak pattern has been used to detect rubratoxin B, as it is known that the rubratoxin are unstable [68,69]. To dereplicate the rubratoxin artefacts, rubratoxins A ($C_{26}H_{32}O_{11}$, M_r 520.1945) and B ($C_{26}H_{30}O_{11}$, M_r 518.5176) were dissolved in acetonitrile only minutes before injection, now showing only one peak from each standard, with accurate masses and UV spectra matching literature data [52]. Both spectra were dominated by $[M+H]^+$, $[M+NH_4]^+$, $[M+H+CH_3CN]^+$, $[M+Na+CH_3CN]^+$ an $[M+H\text{-}nH_2O]^+$ all ions confirmed by their accurate mass. The two major artefact peaks in the rubratoxin A both showed a $[M+H]^+$ ion (assignment confirmed by the presence of water loss ions, as well as sodium and ammonium adducts) at m/z 553.2266 and the two major chromatographic peaks in rubratoxin B showed a $[M+H]^+$ ion at m/z 551.2148. These ions could only be $C_{27}H_{37}O_{12}$ (calc. M_r 553.2285) and $C_{27}H_{35}O_{12}$ (calc. M_r 551.2129), respectively, indicating a gain of CH_4O, this gain was strangely also observed when the components were dissolved in acetonitrile, most likely originating from traces of methanol in the HPLC system (used as sample and cleaning solvent).

4.3. Stachybotrys

During work on the chemistry of *S. chartarum* isolates from mouldy buildings, detection by LC–UV of simple and macrocyclic trichothecenes as well as the atranones has been obscured the very high quantities of spirocyclic drimanes which is always produced by this genus. Hence, the spirocyclic drimanes had to be removed by solid-phase extraction on poly(ethyleneimine) (PEI) silica [70] prior to LC–UV detection [46] or the trichothecenes detected as their parent alcohols by GC–MS–MS [50].

Using an LC–MS method with low cone voltages to reduce in-source fragmentation (Table 3), trichothecenes, spirocyclic drimanes and the atranones can be detected in one go. Fig. 5 shows LC–UV–MS chromatograms of a satratoxin producing *S. chartarum* isolate after the extract was cleaned-up on PEI silica to obtain reasonable UV spectra. This sample contained a macrocyclic trichothecene previously assigned as a roridin E isomer based one the UV spectrum (Fig. 5D), as it show two absorptions, strongly indicating a 2′,3′-C=C bond (only seen from verrucarins J and L, and the roridins E, H and J and their isomers). However, from the mass spectrum, $[M+H]^+$ and $[M+NH_4]^+$ indicated hydroxyroridin E also supported by a an almost 4 min shorter retention time than roridin E. A search in CAS reveals one component with these features, 16-hydroxyroridin E [71], but as the detected hydroxy-

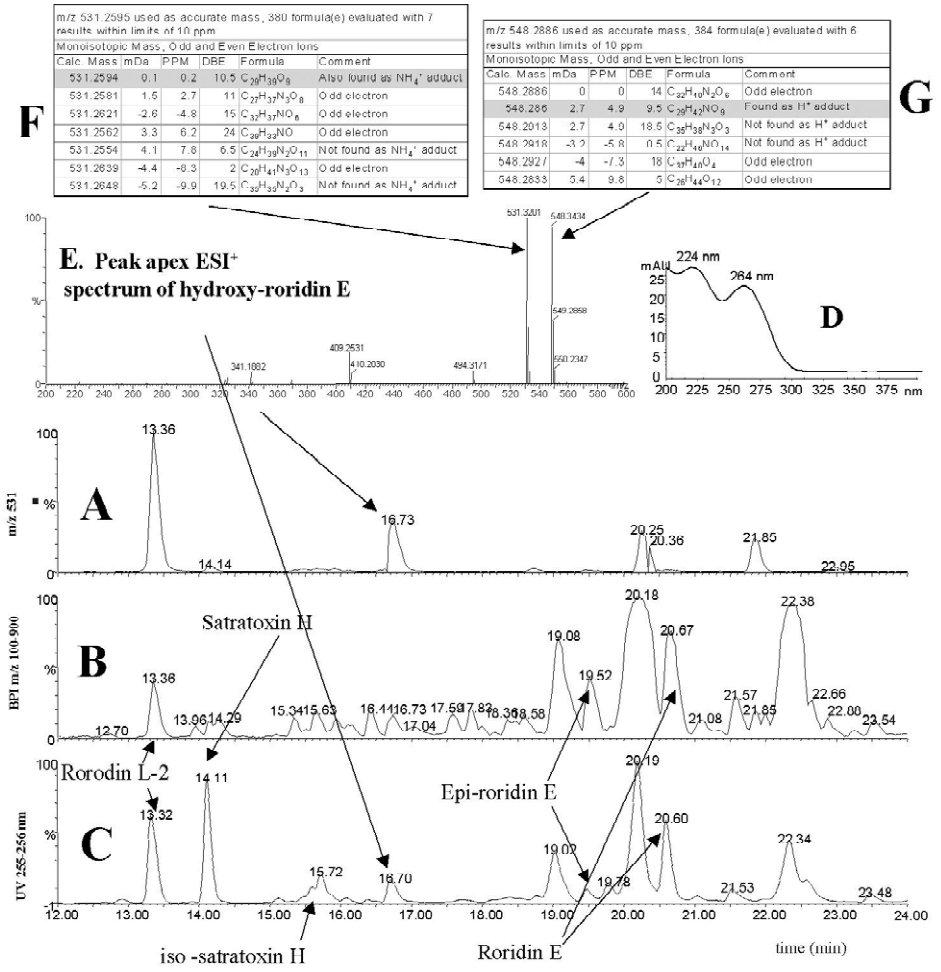

Fig. 5. Partial identification of the novel hydroxyroridin E analogue, from *Stachybotrys chartarum* grown for 14 days on potato sucrose agar [53] (1.5 cm^2 culture extracted) and cleaned up on polyethyleneimine silica. (A) Extracted m/z 531 chromatogram, $[M+H]^+$, (B) base-peak chromatogram, and (C) UV 255–265 nm trace. (D) UV spectrum of this metabolite, (E) peak apex ESI^+ spectrum. (F) and (G) Elementary composition calculations of the $[M+H]^+$ and $[M+NH_4]^+$ ions with masses taken from the tail of the peak.

roridin E also showed fragments at m/z 231 and 249 at higher cone voltages (detected from all di-esters of verrucarol), this component is probably not 16-hydroxyverrucarol, but rather have the extra oxygen on the macrocyclic ring.

5. Conclusion

The present method presents a fast and powerful dereplication tool for many secondary metabolites from micro-fungi, by providing data >400 metabolites to be used without having them as reference components. This paper also gives guidance on which metabolites groups that can be analysed by LC with DAD or positive ESI-MS detection.

The use of high-resolution oaTOF-MS, is an efficient tool for determining the molecular composition of many target components, and by calculation of accurate masses from several adduct and fragment ions the molecular composition can be verified. The use of UV spectra is still valuable for identifying components based on older literature and/or differentiating isomers.

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