

Review

Diversity of Pyrrolizidine Alkaloids in the Boraginaceae Structures, Distribution, and Biological Properties

Assem El-Shazly ¹ and Michael Wink ^{2,*}

¹ Department of Pharmacognosy, Faculty of Pharmacy, Zagazig University, Zagazig 44519, Egypt; E-Mail: assemels2002@yahoo.co.uk

² Institute of Pharmacy and Molecular Biotechnology, Heidelberg University, Im Neuenheimer Feld 364, 69120 Heidelberg, Germany

* Author to whom correspondence should be addressed; E-Mail: Wink@uni-hd.de; Tel.: +49 6221-544881; Fax: 0049 6221-544884.

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Abstract: Among the diversity of secondary metabolites which are produced by plants as means of defence against herbivores and microbes, pyrrolizidine alkaloids (PAs) are common in Boraginaceae, Asteraceae and some other plant families. Pyrrolizidine alkaloids are infamous as toxic compounds which can alkylate DNA and thus cause mutations and even cancer in herbivores and humans. Almost all genera of the family Boraginaceae synthesize and store this type of alkaloids. This review reports the available information on the present status (literature up to early 2014) of the pyrrolizidine alkaloids in the Boraginaceae and summarizes the topics structure, distribution, chemistry, chemotaxonomic significance, and biological properties.

Keywords: pyrrolizidine alkaloids; Boraginaceae; distribution; structures; NMR spectroscopy; mass spectrometry; biological properties

1. Introduction

Pyrrolizidine alkaloids (PAs) are common secondary metabolites in Boraginaceae, Fabaceae (tribe Crotalariae) and Asteraceae (tribe Senecioneae) and serve as chemical defence compounds mainly against herbivores [1,2]. Several PA producing plants grow as weeds and therefore occur widely in agricultural production system throughout the world. They can enter the human food chain as a result

of co-harvesting PA containing plants with edible grains. When bees visit areas, in which PA plants are abundant, PAs can be transferred into honey because nectar and pollen of PA plants contain alkaloids [3]. PA-contaminated human food can include cereals, milk, honey, eggs, and meat. In addition a PA-intake can occur when herbal teas and traditional medicines of the PA-containing plants are consumed [4–17].

Chronic health problems have been attributed to the presence of PAs in these products. The long-term toxicity is due to the conversion of pyrrolizidine alkaloids to the corresponding pyrrole derivatives which are highly reactive; they can alkylate DNA and have the ability to form DNA cross-linkage. As a consequence DNA replication is interrupted and mutations can occur, which can lead to liver and kidney cancer [6,18,19]. The ring nucleus (necine base) with a double bond in the 1:2 position is essential for genotoxic effects of these alkaloids. PAs are bitter and modulate several neuroreceptors, including 5-HT receptors [20–22] which can induce immediate food avoidance in herbivores.

Many of the PAs have been shown to exhibit hepatotoxic, pulmotoxic, haemolytic, antimitotic, teratogenic, mutagenic and carcinogenic effects [22–36].

Plants of the family Boraginaceae are famous for the production of PAs. These alkaloids occur as free necines (either the necine base heliotridine or retronecine) or as a mixture of free bases and their *N*-oxides. They can form single esters (monoester) at C-9 or C-7, open chain diesters at both C-7 and C-9 of the necine base, or in rare cases macrocyclic diesters linking C-7 with C-9 (Figures 1 and 2).

Several reviews on the occurrence of PAs have been published already [23–32,35,37–39] In the present review, we have made a complete review of PAs in Boraginaceae and have added also older records which were not covered so far. Tables 1 and 2 list the distribution of PAs in the Boraginaceae (a last comprehensive review was published by Hartmann and Witte [29]). GLC and GLC-MS data are tabulated in Table 3. For NMR data, we have only included NMR data of new PAs from the Boraginaceae in the time frame 1991–2013 for ^{13}C (Table 4) and 1994–2013 for ^1H (Table 5).

Figure 1. Basic structures of pyrrolizidine alkaloids in Boraginaceae.

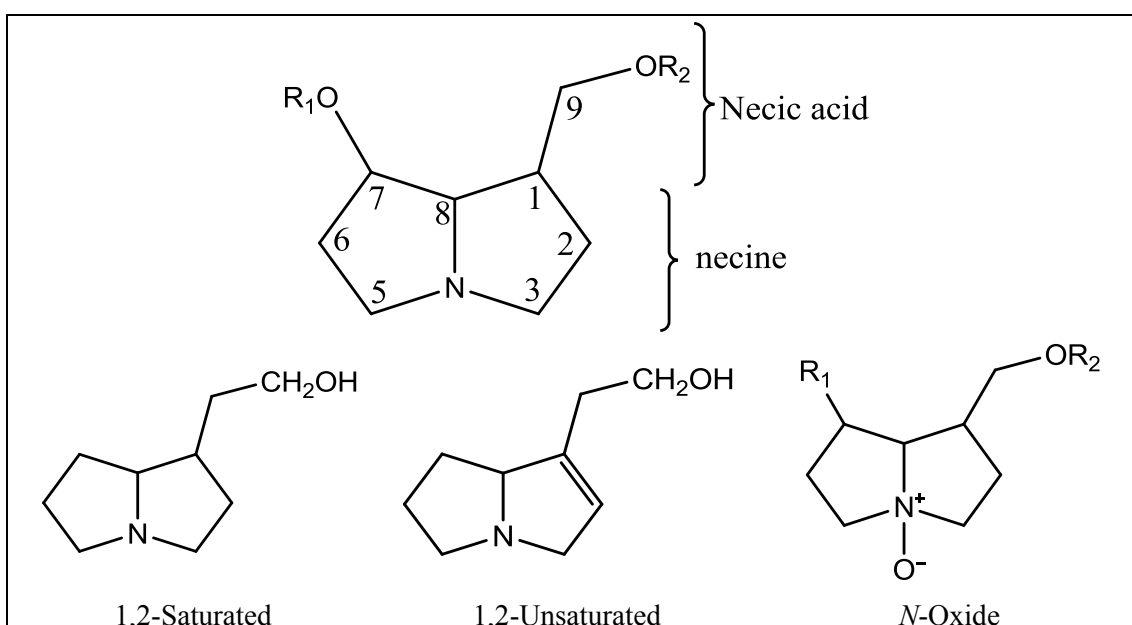
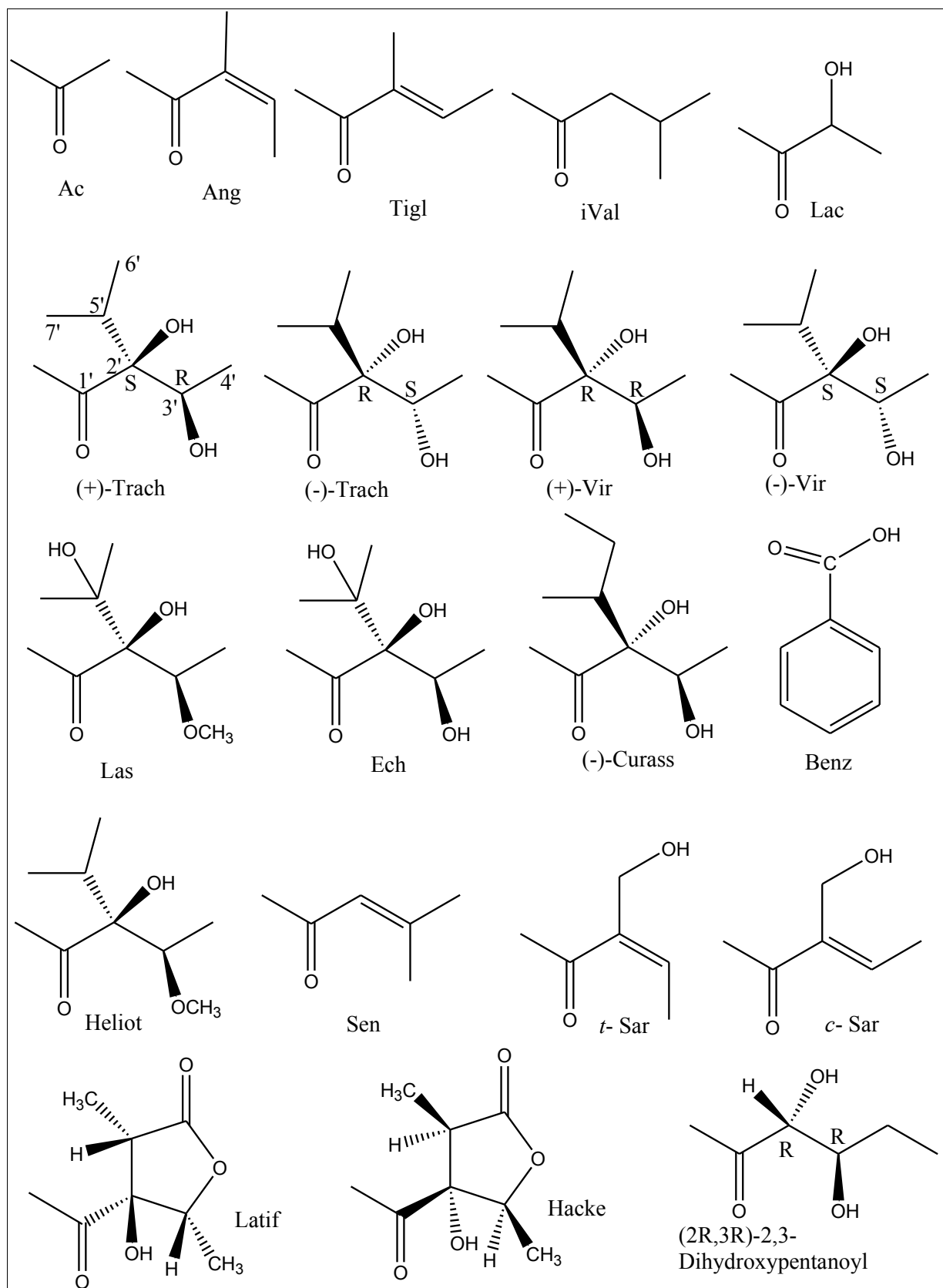


Figure 2. Necic acids occurring in pyrrolizidine alkaloids of Boraginaceae.

Ac = Acetic acid; Ang = Angelic acid; Benz = Benzoic acid; Curass = Curassavic acid; Heliot = Heliotric acid; Ech = Echimidinic acid; Hacke = Hackelic acid; iVal= isovaleric acid; Lact = Lactic acid; Las = Lasiocarpic acid; Latif = Latifolic acid; Sar = sarracine acid; Sen = Senecioic acid; Trach = Trachelanthic acid; Tigl = Tiglic acid; Vir = Viridifloric acid.

Table 1. List of plant species of the Boraginaceae containing PAs.

Species	Pyrrolizidine alkaloids	References
<i>Alkanna orientalis</i>	7-Angeloylretronecine, 9-angeloylretronecine, 7-tigloylretronecine, 9-tigloylretronecine, 7-seneioylretronecine, 9-senecioylretronecine, triangularine, dihydroxytriangularine, triangularicine, dihydroxytriangularicine, 7-angeloyl-9-(hydroxypropenoyl) retronecine, 7-tigloyl-9-(hydroxypropenoyl) retronecine, 7-angeloyl-9-(2,3-dihydroxypropanoyl) retronecine, 7-tigloyl-9-(2,3-dihydroxypropanoyl) retronecine.	[40,41]
<i>A. tinctoria</i> (<i>A. tuberculata</i>)	7-Angeloylretronecine, 7-tigloylretronecine, 9-tigloylretronecine, triangularine, dihydroxytriangularine, triangularicine, dihydroxytriangularicine, 7-acetyl-9-sarracinoylretronecine, 7-angeloyl-9-(hydroxypropenoyl) retronecine, 7-tigloyl-9-(hydroxypropenoyl) retronecine, 7-angeloyl-9-(2,3-dihydroxypropanoyl) retronecine, 7-tigloyl-9-(2,3-dihydroxypropanoyl) retronecine.	[40,41]
<i>Amsinckia carinata</i>	Echiumine, furcatine, 3'-acetylfurcatine, intermedine, 7-acetylintermedine, lycopsamine, myoscorpine, supinine.	[42]
<i>A. douglasiana</i>	Amabiline, cynaustiline, intermedine, lycopsamine, tessellatine, 9-(3'-acetylviridifloryl)turniforcidine.	[42,43]
<i>A. eastwoodiae</i>	Amabiline, intermedine, 3'-acetylintermedine, echiumine, lindelofine, lycopsamine, supinine, tessellatine.	[42]
<i>A. furcata</i>	Furcatine, intermedine, 3'-acetylfurcatine, lycopsamine, supinine, tessellatine.	[42]
<i>A. grandiflora</i>	Amabiline, intermedine, lycopsamine, 3'-acetyllycopsamine, 7-acetyllycopsamine, tessellatine, 9-acetyltessellatine.	[42]
<i>A. hispida</i>	Echiumine, intermedine, lycopsamine.	[44]
<i>A. intermedia</i>	Echiumine, intermedine, lycopsamine, sincamidine.	[44]
<i>A. lunaris</i>	Lycopsamine, 3'-acetyllycopsamine, intermedine, supinine, tessellatine, 9'-acetyltessellatine.	[42]
<i>A. lycopsoides</i>	Amabiline, echiumine, intermedine, 3'-acetylintermedine, lycopsamine, supinine, tessellatine.	[42,44]
<i>A. lycopsoides</i> × <i>menziesii</i> var. <i>intermedia</i>	Amabiline, intermedine, 3'-acetylintermedine, lycopsamine, supinine, tessellatine.	[42]
<i>A. menziesii</i>	Intermedine, lycopsamine, 3'-acetyllycopsamine, 7-acetyllycopsamine, 3',7-diacetyllycopsamine.	[45]
<i>A. menziesii</i> var. <i>intermedia</i>	Amabiline, cynaustaine (or stereoisomer), echiumine, 3'-acetylechiumine, intermedine, 3'-acetylintermedine, 7-acetylintermedine, 3',7-diacetylintermedine, lindelfoline, lycopsamine, 3'-acetyllycopsamine, 7-acetyllycopsamine, myscorpine, 3'-acetylmyscorpine, supinine, symlandine, tessellatine.	[42,43]
<i>A. retrosa</i>	Amabiline, intermedine, 3'-acetylintermedine, lycopsamine, myscorpine, 3'-acetylmyscorpine, supinine, tessellatine.	[42]
<i>A. spectabilis</i> var. <i>microcarpa</i>	Intermedine, 3'-acetylintermedine, lindelofine, lycopsamine, myscorpine, supinine, tessellatine.	[42]
<i>A. spectabilis</i> var. <i>spectabilis</i>	Intermedine, 3'-acetylintermedine, lindelofine, lycopsamine, supinine.	[42]

Table 1. Cont.

Species	Pyrrolizidine alkaloids	References
<i>A. spectabilis</i> var. <i>nicolai</i>	Intermedine, lindelofine, lycopsamine, tessellatine, trachelanthamine, supinine.	[42]
<i>A. tessellata</i>	Intermedine, lycopsamine, 3'-acetylintermedine, 3'-acetyllycopsamine, 7-acetylintermedine, 7-acetyllycopsamine, 3',7-diacetylintermedine, 3'-7-diacetyllycopsamine.	[46]
<i>A. tessellata</i> var. <i>gloriosa</i>	Amabiline, intermedine, lycopsamine, supinine, tessellatine, trachelanthamine, viridiflorine, 3'-acetylviridiflorine.	[42,43]
<i>A. tessellata</i> var. <i>tessellata</i>	Amabiline, intermedine, lycopsamine, 3'-acetyllycopsamine, tessellatine, 3'-acetyltessellatine, 9-acetyltessellatine, 9,3'-acetyltessellatine, 9-(3'-acetylviridifloryl)-turniforcidine.	[42]
<i>A. vernicosa</i>	Furcatine, intermedine, lycopsamine, supinine, 7-trachelanthyl retronecine.	[42]
<i>Anchusa arvensis</i> (= <i>Lycopsis arvensis</i>)	Echinatine, intermedine, 7-acetylintermedine, lycopsamine, 7-acetyllycopsamine, 3',7-diacetylintermedine (or its isomer 3',7-diacetyllycopsamine), supinine, 9-acetyltrachelanthamidine, 9-angeloyltrachelanthamidine.	[40,47]
<i>A. hispida</i> (= <i>Gastrocotyle hispida</i>)	7-Angeloylheliotridine, intermedine, lycopsamine, 7-acetyllycopsamine, retronecine, trachelanthamine and its isomer.	[40]
<i>A. milleri</i>	Heliotridine, 7-angeloylheliotridine, rinderine, retronecine, supinine, viridiflorine, 9-curassavoylheliotridine, 7-acetyl-9-curassavoylheliotridine.	[40]
<i>A. officinalis</i>	Intermedine, curassavine, lycopsamine, 7-acetyllycopsamine.	[47–49]
<i>A. strigosa</i>	Heliotridine 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester, platyneine N-oxide 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester, retronecine 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester and its N-oxide, retronecine 2S-hydroxy-2S(1R-hydroxyethyl)-4-methyl-pentanoyl ester and its N-oxide, retronecine 2S-hydroxy-2S(1S-hydroxyethyl)-[1'S-hydroxyethyl]-4-methyl-pentanoyl ester, supinidine N-oxide 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester, trachelanthamidine 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester.	[50,51]
<i>Arnebia decumbens</i>	7-angeloylrtronecine, 9-angeloylrtronecine, 7-tigloylrtronecine, 9-tigloylrtronecine, europine, heliotrine, lycopsamine, rinderine, supinine.	[52]
<i>Arnebia euchroma</i>	7-angeloylrtronecine, 9-angeloylrtronecine	[53]
<i>A. hispidissima</i>	Echimidine, monocrotaline.	[54]
<i>Asperugo procumbens</i>	Amabiline (or supinine), echinatine.	[47]
<i>Borago officinalis</i>	Amabiline, intermedine, 7-acetylintermedine, lycopsamine, 7-acetyllycopsamine, supinine, thesinine, thesinine-4'-O- β -D-glucoside.	[55,56]
<i>Caccinia crassifolia</i>	Supinine, Heliotridine or retronecine trachelanthate.	[57]

Table 1. Cont.

Species	Pyrrolizidine alkaloids	References
<i>C. glauca</i>	Retronecine 7:9 -dibenzoate.	[58]
<i>Cerintho glabra</i>	Lycopsamine, 3'-acetyllycopsamine, 7-acetyllycopsamine, 3',7-diacetyllycopsamine, supinine, 7-hydroxymethyl butyryl-9-iridifloryl-retronecine (or isomer).	[59]
<i>Cerintho minor</i>	Intermedine, 7-angeloylretronecine, 9-angeloyl-7-iridiflorylretronecine, lycopsamine.	[60,61]
<i>Cordia myxa</i>	macrophylline	[62]
<i>C. sinensis</i>	floridanine	[62]
<i>Cryptantha cana</i>	Intermdine, 3'-acetylintermedine, 7-acetylntemedine, lycopsamine, 3'-acetyllycopsamine, 7-acetyllycopsamine.	[63]
<i>C. clevelandii</i>	Intermdine, 3'-acetylintermedine, echiumine, 2",3"-epoxyechiumine, <i>thero</i> -2',3' dihydroxyechiumine, <i>erytho</i> -3"-chloro-2"-hydroxyechiumine.	[63]
<i>C. confertiflora</i>	Amabiline, intermedine, lycopsamine, tessellatine, 9-acetyltessellatine.	[63]
<i>C. crassipes</i>	Lycopsamine, intermedine and their 3'-acetyllycopsamine, 3'-acetylintermedine, 7-acetyllycopsamine, 7-acetylintermedine, amabiline, echiumine, dihydroechumine, echimiplate, lepanthine.	[64]
<i>C. fendleri</i>	7-Angeloylretronecine, 9-angeloylretronecine, latifoline, neolatifoline.	[63]
<i>C. flava</i>	Intermedine, 3'-acetylintermedine, 7-acetylntemedine, lycopsamine, 3'-acetyllycopsamine, 7-acetyllycopsamine.	[63]
<i>C. inequata</i>	Echimidine, acylechimidine, echiuplatine, methylechiuplatine, lycopsamine, intermedine, dihydroxyechiumine.	[65]
<i>C. jamesii</i>	Intermedine, lycopsamine, 3'- acetyllycopsamine, 7-aetyllyopsamine.	[66]
<i>C. leiocarpa</i>	7-Angeloylretronecine, 9-angeloylretronecine, echiumine, intermedine, 3'-acetylintermedine, 2",3"-epoxyechiumine, <i>thero</i> -2',3'-dihydroxyechiumine, <i>erytho</i> -3"-chloro-2"-hydroxyechiumine	[63]
<i>C. thyrsoflora</i>	Intermedine, 3'-acetylintermedine, 7-acetylntemedine, lycopsamine, 3'-acetyllycopsamine, 7-acetyllycopsamine	[63]
<i>C. utahensis</i>	Cryptanthine	[65]
<i>C. virgata</i>	Intermedine, 3'-acetylintermedine, 7-acetylntemedine, lycopsamine, 3'-acetyllycopsamine, 7-acetyllycopsamine	[63]
<i>C. virginensis</i>	Amabiline, intermedine, lycopsamine, tessellatine.	[63]
<i>Cynoglossum amabile</i>	Amabiline, echinatine, 7-acetylechinatine, lycopsamine, rinderine, supinine. 9-angeloylretronecine, 9-angeloyl-7-iridiflorylretronecine,	[60,67,68]
<i>C. australe</i>	Cynausine, cynaustraline.	[68]
<i>C. clandestinum</i>	9-Angeloyl-7-iridiflorylretronecine, trachelanhamine	[60]
<i>C. columnae</i>	N-oxides of echintine, rinderine, 3'-acetylirinderine, 7-tigloyl-9-(2-deoxy-2-methyl)echimidinyl heliotridine.	[69]

Table 1. Cont.

Species	Pyrrolizidine alkaloids	References
<i>C. creticum</i>	Cynoglossamine, echinatine, 3'-acetylechinatine, heliosupine, 3'-acetylheliosupine, 7-angeloylheliotridine, 7-angeloyl-9-(methylbutyryl) heliotridine, 7 α -angeloyl-1-chloromethyl-1,2-dehydropyrrolizidine, 7-senecioylheliotridine, rinderine, 3'-acetylrenderine, supinine, trachelanthamine (or isomer).	[70–72]
<i>C. furcatum</i> (<i>C. zeylanicum</i>)	Echinatine, <i>isoechinatine</i> , neocoromandaline, cynaustraline, lactodine, viridinatine	[73–76]
<i>C. germanicum</i>	Echinatine, viridiflorine.	[77]
<i>C. glochidiatum</i>	Amabiline	[78]
<i>C. lanceolatum</i>	Cynaustine, cynaustraline.	[78]
<i>C. latifolium</i>	7-Angeloylheliotridine, latifoline.	[79]
<i>C. macrostylum</i>	Echinatine, heliosupine.	[80]
<i>C. montanum</i>	Cynaustine, cynaustraline, echinatine, heliosupine.	[81]
<i>C. nervosum</i>	Heliotrine, echinatine, rinderine and their N-oxides.	[82]
<i>C. officinale</i>	Echinatine, 3'-acetylechinatine, 7-angeloylechinatine, heliosupine, 3'-acetylheliosupine, 7-angeloylheliotridine, 7-angeloyl-1-formyl-6,7-dihydro-5H-pyrrolizidine, 7-angeloyl-9-(2-methylbutyryl)heliotridine, 7-angeloyl-9-(2,3-dihydroxybutyryl) heliotridine, 7-tigloylheliotridine, rinderine, 7-angeloylrinderine, trachelanthamine, viridiflorine.	[67,83,84]
<i>C. pictum</i>	Echinatine, heliosupine, pictumine.	[85]
<i>C. viridiflorum</i>	Heliosupine, viridiflorine.	[86]
<i>Echium amoenum</i>	Echimidine, echimidine isomer (tigloyl), 7-angeloylretronecine, 7-tigloylretronecine.	[87]
<i>E. angustifolium</i>	Echimidine	[88]
<i>E. diffusum</i>	Heliotridine or retronecine esters.	[28]
<i>E. glomeratum</i>	7-Angeloylretronecine, 9-angeloylretronecine, (7 <i>S</i> ,8 <i>R</i>)petranine, (7 <i>S</i> ,8 <i>S</i>)petranine.	[89]
<i>E. horridum</i>	Echimidine, echimidine isomer (tigloyl), lycopsamine, 7-acetyllycopsamine, 7-angeloyllycopsamine, 7-tigloyllycopsamine, 7-angeloylretronecine, 7-tigloylretronecine, 7-angeloyl-9-(2-methylbutyryl)retronecine, 7-tigloyl-9-(2-methylbutyryl) retronecine, 7-angeloyl-9-(2, 3-dihydroxybutyryl)retronecine, 7-tigloyl-9-(2, 3-dihydroxybutyryl)retronecine, uplandicine.	[90]
<i>E. humile</i>	Echimidine, echihumiline, lycopsamine, 7-acetyllycopsamine, 7-seneciolylycopsamine, pycnanthine, 7-seneiolyretronecine, 9-seneiolyretronecine, 7-(2-methylbutyryl)retronecine, 7-(methylbutyryl)-9-(2,3-dihydroxybutyryl)retronecine, 7-(2-methylbutyryl)-9-echimidinylretronecine.	[91]

Table 1. Cont.

Species	Pyrrrolizidine alkaloids	References
<i>E. hypertropicum</i>	Echimidine, echihumiline, 7-(2-methylbutyryl)-9-echimidinylretronecine, 7-seneciolyretronecine, 9-angeloylretronecine, lycopsamine, 7-acetyl-lycopsamine	[92]
<i>E. italicum</i>	Echimidine	[28]
<i>E. lycopsis</i> (= <i>E. plantagineum</i>)	Echimidine, echiumine, uplandicine, lycopsamine, intermedine, echimplatine, echiuplatine, 3'-acetylintermidine, 3'-acetyllycopsamine, 3'-acetylechiumine, 9-angeloylretronecine, leptanthine.	[4,93,94]
<i>E. pininana</i>	Echimidine, ehiupinine, 3'-aetylintermidine, hydroxymyoscorpine, myoscorpine.	[95]
<i>E. rauwolfii</i>	Echimidine, echimidine isomer (tigloyl), 7-acetyllycopsamine, 7-angeloyllycopsamine, 7-tigloyllycopsamine, 7-angeloylretronecine, 7-tigloylretronecine, 7-angeloyl-9-(2-methylbutyryl)retronecine, 7-tigloyl-9-(2-methylbutyryl)retronecine, 7-angeloyl-9-(2, 3-dihydroxybutyryl)retronecine, 7-tigloyl-9-(2, 3-dihydroxybutyryl)retronecine, uplandicine.	[90]
<i>E. sericeum</i>	Echimidine, symlandine (or symphytine).	[54]
<i>E. setosum</i>	Echimidine, echimidine isomer (tigloyl), 7-angeloylretronecine, 7-tigloylretronecine, 9-angeloylretronecine, 9-tigloylretronecine, 7-angeloyl-9-(2-methylbutyryl) retronecine, 7-tigloyl-9-(2-methylbutyryl) retronecine, 7-angeloyl-9-(2,3-dimethylbutyryl) retronecine, 7-angeloyl-9-(2,3-dihydroxybutyryl) retronecine, uplandicine.	[96]
<i>E. simplex</i>	7-Angeloylretronecine, 9-angeloylretronecine.	[61]
<i>E. stenosphon</i> Webb subsp. <i>stenosphon</i>	Echimidine, 7-(2-methylbutyryl)-9-echimidinylretronecine	[92]
<i>E. tuberculatum</i>	Echimidine, 7-angeloyl-9-iridiflorylretronecine, 7-iridiflorylretronecine.	[60]
<i>E. vulgare</i>	Asperumine, heliosupine, 3'-acetylheliosupine, Echinatine, echiuplantine, leptanthine, echimiplantine, echivulgarine, vulgarine, 7-O-acetylvulgarine, echimidine, echimidine isomer (tigloyl ?), 3'-acetylechimidine, 5'-acetylechimidine, echihumiline, retronecine, 7-angeloylretronecine, 9-angeloylretronecine, 7-tigloylretronecine, 9-tigloylretronecine, 7-(2-methylbutyryl) retronecine, 9-(2-methylbutyryl) retronecine, 7-angeloyl-9-(2-methylbutyryl) retronecine, 7-tigloyl-9-(2-methylbutyryl) retronecine, 7-angeloyl-9-(2, 3-di methylbutyryl) retronecine, 7-tigloyl-9-(2, 3-dihydroxybutyryl)retronecine, uplandicine	[11,96–98]
<i>E. wildpretti</i>	Echimidine and its N-oxide.	[99]
<i>Ehretia aspera</i>	Ehretinine	[100]
<i>Eritrichium rupestre</i>	7-Angeloylretronecine, 7-angeloyl-9-iridiflorylretronecine, 7-iridiflorylretronecine	[60]
<i>Hackelia californica</i>	Hackelidine, longitubine, 7-acetylhackelidine, 9-latifolylretronecine, 7-acetyl-9-latifolylretronecine	[101,102]

Table 1. Cont.

Species	Pyrrolizidine alkaloids	References
<i>H. floribunda</i>	Latifoline and its N-oxide.	[103]
<i>H. longituba</i>	Latifoline, neolatifoline, longitubine, 7-angeloylretronecine, 9-angeloylretronecine.	[104]
<i>Heliotropium acutifolium</i>	Heliotrine	[105]
<i>H. amplexicaule</i>	Indicine	[29]
<i>H. angiospermum</i>	Subulacine, lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>H. arbainense</i>	Europine, heliotrine, lasiocarpine.	[71]
<i>H. arborescens</i> (= <i>H. peruvianum</i>)	Indicine, 3'-acetylcindicine, lasiocarpine.	[107]
<i>H. arguzioides</i>	Heliotrine, trichodesmine.	[28]
<i>H. bacciferum</i>	Europine, heliotrine, heleurine and their N-oxides, supinine.	[108,109]
<i>H. bovei</i>	Europine, 7-acetyeuropine, lasiocarpine, 5'-acetyl lasiocarpine, lasiocarpine N-oxide, 5'-acetyl lasiocarpine N-oxide.	[110]
<i>H. bracteatum</i>	Helibractinecine, retronecine, helibracteatinine, helibracteatine	[111,112]
<i>H. bursiferum</i>	7-Angeloylretronecine.	[113]
<i>H. circinatum</i>	7-angeloylheliotrine, echinatine, europine, heleurine, heliotrine, lasiocarpine.	[114]
<i>H. confertifolium</i>	lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>H. crassifolium</i>	Ilamine, europine and their N-oxides.	[115]
<i>H. curassavicum</i>	Coromandaline, coromandalinine, curassavine, curassavinine, curassanecine, heliocurassavine, heliocurassavinine, heliocurassavicine, heliocoromandaline, heliovicine, 7-angeloylheliotridine, trachelanthamidine, retronecine, supinidine.	[106,116–118]
<i>H. curassavicum</i> var. <i>argentium</i>	9-(3'-isovaleryl) viridifloryl retronecine, 9-(3'-acetyl) viridifloryl retronecine.	[119]
<i>H. curassavicum</i> var. <i>curassavicum</i>	9-(3'-isovaleryl) viridifloryl retronecine, 9-(3'-acetyl) viridifloryl retronecine.	[119]
<i>H. dasycarpum</i>	heliotrine	[120]
<i>H. digynum</i> (<i>H. luteum</i>)	Europine, heliotrine, 7-angeloylheliotrine, lasiocarpine.	[121]
<i>H. disciforme</i>	Heliotrine, 2'-actylheliotrine, heliotrine N-oxide, heleurine, heliorine N-oxide.	[122]
<i>H. dissitiflorum</i>	Heliotrine, heliotrine N-oxide, europine, 5'-deoxylasioscarpine.	[123]
<i>H. eichwaldii</i>	Heliotrine, 7-angeloylheliotrine, lasiocarpine.	[124]
<i>H. esfandiarii</i>	Europine, europine N-oxide.	[125]

Table 1. Cont.

Species	Pyrrrolizidine alkaloids	References
<i>H. europaeum</i>	Europine, acetyeuropine, heleurine, heliotrine, 7-angeloylheliotrine, lasiocarpine, 6-acetylasiocarpine, heliotrine N-oxide, dehydroheliotrine, 5'-acetylasiocarpine N-oxide, N-(dihydropyrrrolizinomethyl)-heliotrine, supinine.	[126,127]
<i>H. floridum</i>	Floridine, floridinine, floridimine, heliovicine, 3'-acetyltrachelanthamine.	[128]
<i>H. foliosissimum</i>	lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>H. fruticosum</i>	lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>H. hirsutissimum</i>	Europine, heliotrine, heleurine, lasiocarpine, 3'-acetylasiocarpine, 5'-acetylasiocarpine, supinine, N-oxides of acetylasiocarpine, 3'-acetylheliosupine.	[29,129]
<i>H. indicum</i>	Echinatine, helindicine, heliotrine, heleurine, indicine, acetylindicine, indicinine, lasiocarpine, lycopsamine, rinderine, supinine, lindelofidine, retronecine, supinidine, trachelanthamine.	[106,116,130–132]
<i>H. keralense</i>	Intermedine, <i>isolycopsamine</i> , retronesine.	[133]
<i>H. lasiocarpum</i>	Heliotrine, lasiocarpine.	[29]
<i>H. marifolium</i>	Europine, heliotrine, indicine, lasiocarpine.	[29]
<i>H. maris mortui</i>	Europine, lasiocarpine.	[29,71]
<i>H. megalanthum</i>	Lycopsamine, megalanthonine.	[134]
<i>H. molle</i>	subulacine	[29]
<i>H. olgae</i>	Heliotrine, incanine.	[135]
<i>H. ovalifolium</i>	Heliofoline, retronecine.	[136]
<i>H. peruvianum</i>	Rinderine	[29]
<i>H. popovii</i> subsp. <i>gillianum</i>	Heliotrine	[28]
<i>H. procumbens</i>	Lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>H. queretaroanum</i>	Lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>H. racemosum</i>	Lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>H. ramosissimum</i>	Heliotrine	[28]
<i>H. rotundifolium</i>	Europine, 5'-acetyeuropine, heliotrine, lasiocarpine.	[137,138]
<i>H. scabrum</i>	Heliscabine, retronecine.	[139]
<i>H. sessei</i>	Lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>H. spathulatum</i>	Amabiline, coromandaline, coromandalinine, heliovicine, curassavinine, curassavine, heliospathine, heliospathuline, lindelofidine, retronecine, supinidine, trachelanthamidine.	[116,140]

Table 1. Cont.

Species	Pyrrolizidine alkaloids	References
<i>H. steudneri</i>	Lycopsamine	[27]
<i>H. strigosum</i>	Strigosine, trachelanthamidine	[25,141]
<i>H. suaveolens</i>	Echinatine, europine, heliotrine, lasiocarpine.	[29]
<i>H. subulatum</i>	Subulacine; retronecine, heliotrine, 7-angeloylheliotridine	[142]
<i>H. supinum</i>	Echinatine, heliosupine, heliotrine, 7-angeloylheliotridine (and its trachelanthic and viridifloric esters), lasiocarpine, supinine.	[27,143]
<i>H. ternatum</i>	subulacine	[27]
<i>H. transalpinum</i>	Intermedine, indicine, lycopsamine, rinderine, 3'-acetylrinderine, supinine.	[144]
<i>H. transalpinum</i> var. <i>transalpinum</i>	Transalpinecine, subulacine.	[145]
<i>H. transoxanum</i>	Heliotrine	[105]
<i>H. wigginsii</i>	Lindelofidine, retronecine, supinidine, trachelanthamidine.	[106]
<i>Lappula glochidiata</i>	Echinatine	[146]
<i>L. intermedia</i> (<i>Echinospermum</i> <i>intermedium</i>)	Lasiocarpine	[147]
<i>L. myosotis</i>	Intermedine, lycopsamine, 7-acetylintermedine, 7-acetyllycopsamine.	[35,148]
<i>L. spinocarpos</i>	Amabiline, intermedine, 7-angeloylheiortridine, 9- heliotrinoylretronecine, lycopsamine, 7-acetyllycopsamine, retronecine, trachelanthamine, supinine, viridiflorine.	[40]
<i>Lindelofia anchusoides</i> (<i>L. macrostyla</i>)	Lindelofamine, lindelofine.	[28]
<i>L. angustifolia</i>	Amabiline, echinatine	[78]
<i>L. longiflora</i>	Echinatine and its N-oxide.	[149]
<i>L. olgae</i>	Viridiflorine	[150]
<i>L. pterocarpa</i>	Viridiflorine	[151]
<i>L. spectabilis</i>	Echinatine, 3'-acetylechinatine, monocorotaline.	[124]
<i>L. stylosa</i>	Echinatine, lindelofine, viridiflorine.	[135]
<i>L. tschimganica</i>	Echinatine, carategine, viridiflorine.	[152]

Table 1. Cont.

Species	Pyrrolizidine alkaloids	References
<i>Lithospermum canesens</i>	Canesine, canescenine, 3'-acetycanesine, 3'-acetylcanescenine, lycopsamine, 7-acetyllycopsamine, 7-acetylintermediate.	[153,154]
<i>L. erythrorhizon</i>	Intermedine, myoscorpine, hydroxymyoscorpine.	[155]
<i>L. officinale</i>	Lithosenine, acetylithosenine.	[156]
<i>L. purpureocoeruleum</i>	Lycopsamine	[60]
<i>Macrotomia echioides</i>	Macrotomine	[28]
<i>Mertensia bakeri</i>	Lycopsamine	[157]
<i>M. ciliata</i>	Intermedine, lycopsamine.	[157]
<i>Messerschmidia argentea</i>	Indicine, 3'-acetylindicine, and their N-oxide.	[158]
<i>M. sibirica</i>	Lycopsamine, 9-angeloylretronecine.	[28]
<i>Moltikiopsis ciliata</i> (<i>Lithospermum callosum</i>)	Echinatine, heliotrine.	[108]
<i>Myosotis scorpioides</i> (= <i>M. palustris</i>)	Myoscorpine, symphytine, scorpioidine, 7-acetylscorpioidine.	[159]
<i>M. sylvatica</i>	Heliosupine, 3'-acetylheliosupine, 9-angeloylretronecine, trachelanthamine.	[25]
<i>Neatostema apulum</i>	Amabiline, lycopsamine and their N-oxides.	[160]
<i>Nonnea lutea</i>	7-iridiflorylretronecine	[60]
<i>N. setosa</i>	7-iridiflorylretronecine	[60]
<i>Omphalodes verna</i>	Isoretronocanol or its isomer.	[27]
<i>Onosma alborosea</i>	Intermedine, lycopsamine, 7-acetylintermediate, 7-acetylycopsamine.	[161]
<i>O. alboroseum</i> × <i>sanguinolentum</i>	9-Angeloylretronecine, echimidine, lycopsamine, intermedine, 7-acetylintermediate, 7-acetylycopsamine.	[161,162]
<i>O. arenaria</i>	7-Acetyllycopsamine, 5,6-dihydro-7,9-dimethoxy-7H-pyrrolizine, 7-acetylretronecine, 7-acetyl-9-(2-methylbutryl) retronecine, 7-acetyl-9-(2,3-dimethylbutryl) retronecine, 7-acetyl-9-(2-hydroxy-3-methylbutryl) retronecine, 7-acetyl-9-(2,3-dihydroxybutryl) retronecine, 9-(butyryl-2-ene) supinidine, 3'-acetylsupinine, uplandicine.	[163]
<i>O. arenaria</i> subsp. <i>pennina</i>	Intermedine, lycopsamine, 7-acetylintermediate, 7-acetylycopsamine.	[161]

Table 1. Cont.

Species	Pyrrolizidine alkaloids	References
<i>O. erecta</i>	N-oxides of 7-O-acetylechinate, viridinatine, stereoisomer, 7-epi-echimiplate, onosmerectine.	[164]
<i>O. hetrophyllum</i>	Helioridine, 1-methylene-8 α -pyrrolizidine.	[165]
<i>O. leptantha</i>	Echihumiline, 3'-acetylechihumiline, leptanthine and their N-oxides.	[166]
<i>O. stellulatum</i>	Echimidine, 7-viridiflorylretronecine, heliospathuline, leptanthine, lyopsamine and heir N-oxides, 7-acetylintermedine, dihydroechinate, trachelanthamine, uplandicine.	[60,167]
<i>Paracaryum himalayense</i>	Viridiflorine	[151]
<i>P. intermedium</i>	7-Angeloylheliotridine, 7-seneciylheliotridine, rinderine, 7-angeloylrindrine, 7-seneciylrinderine, viridiflorine.	[40]
<i>P. regulosum</i>	Echinatine, heliosupine, 7-angeloylheliotridine, rinderine, viridiflorine.	[40]
<i>Paracynoglossum imeretinum</i>	Echinatine, heliosupine.	[29]
<i>Pulmonaria obscura</i>	Intermedine, lycopsamine, 7-acetylintermedine, 7-acetylycopsamine.	[168]
<i>Rindera austroechinata</i>	Echinatine, rinderine, 7-angeloylheliotridine	[57,152]
<i>R. baldschuanica</i>	Echinatine, rinderine, trachelanthamine, turkestanine	[152]
<i>R. cyclodonta</i>	Echinatine	[120]
<i>R. echinata</i>	Echinatine, trachelanthamine	[120]
<i>R. oblongifolia</i>	Cerategine, echinatine, turkestanine.	[152]
<i>R. umbellata</i>	7-Angeloyl-9-(+)-trachelanthyl heliotridine, lindelofine, punctanecine, 7-angeloyl heliotridane, 7-angeloyl heliotridine, heliosupine, 9-(+)-trachelanthyl-laburnine, echinatine.	[169]
<i>Solenanthus circinnatus</i>	Echinatine	[151]
<i>S. coronatus</i>	Echinatine	[135]
<i>S. karateginus</i>	Cerategine, echinatine.	[151]
<i>S. turkestanicus</i>	Rinderine, turkestanine.	[135,150]
<i>Symphytum aintabicum</i>	Echimidine	[170]
<i>S. asperum</i>	Echimidine, symphytine, asperumine, echinatine, heliosupine, acetylechimidine (or its isomer), aetyllyopsamine (or its isomer), symviridine	[171,172]
<i>S. bohemiun</i>	Echimidine, lycopsamine, 7-acetylycopsamine, symphytine.	[173]
<i>S. caucasicum</i>	Asperumine, echimidine, echinatine, heliotrine, lasiocarpine.	[174]
<i>S. consolidum</i>	Echimidine, symphytine.	[175]

Table 1. Cont.

Species	Pyrrolizidine alkaloids	References
<i>S. grandiflorum</i>	Echimidine, lycopsamine, symphytine.	[176]
<i>S. ibericum</i>	Echimidine, lycopsamine, symphytine.	[176]
<i>S. officinale</i>	Lycopsamine, 7-acetyllycopsamine, symphytine, echimidine, echinatine, heliosupine, intermedine, 7-acetylintermedine, viridiflorine, symviridine.	[17,162,171,172,177–179]
<i>S. orientale</i>	Anadoline, echimidine, symphytine.	[28]
<i>S. peregrinum</i>	Intermedine, 7-acetylintermedine, lycopsamine, 7-acetyllycopsamine, symphytine.	[27]
<i>S. sylvaticum</i> subsp. <i>sepulcrale</i> var. <i>sepulcrale</i>	Echimidine N-oxide	[170]
<i>S. tanaiense</i>	Echimidine, lycopsamine, 7-acetyllycopsamine, symphytine.	[173]
<i>S. tuberosum</i>	7-Angeloylretronecine; anadoline, echimidine, lycopsamine, 7-acetyllycopsamine, symphytine.	[28,162,176]
<i>S</i> × <i>uplandicum</i>	Echimidine, intermedine, 7-acetylintermedine lycopsamine, 7-acetyllycopsamine, symphytine, symlandine, symviridine, uplandicine.	[172,180]
<i>Tournefortia sarmentosa</i>	Supinine	[28]
<i>T. sibirica</i>	Turneforcine	[29]
<i>T. sogdiana</i>	Echinatine	[57]
<i>Trahlenthus hissaricus</i>	Trachelanthine, trachelanthamine, viridiflorine.	[29]
<i>T. korolkovii</i>	Trachelanthine, trachelanthamidine, trachelanthamine.	[57,150]
<i>Trichodesma africanum</i>	Europine, intermedine, lycopsamine, trichodesmine, retronecine, viridiflorine	[40,71,181]
<i>T. ehrenbergii</i>	Senkirkine, supinine.	[54]
<i>T. incanum</i>	Inanine, trihodesmine.	[46]
<i>T. zeylanicum</i>	Supinine	[182]
<i>Ulugbekia tschimganica</i>	Uluganine	[183]

Table 2. Alkaloid composition of investigated species of Boraginaceae.

Compounds	Sources	References
3'-Acetylcanesine	<i>Lithospermum canesens</i>	[153,154]
3'-Acetylcanescenine	<i>Lithospermum canesens</i>	[153,154]
7-Acetyl-9-curassavoylheliotridine	<i>Anchusa milleri</i>	[40]
7-Acetyl-9-(2,3-dihydroxybutryl) retronecine	<i>Onosma arenaria</i>	[163]
7-Acetyl-9-(2-dimethylbutryl) retronecine	<i>Onosma arenaria</i>	[163]
3'-Acetylechinatine	<i>Cynoglossum creticum</i>	[70]
	<i>Cynoglossum officinale</i>	[67]
	<i>Lindelofia spectabilis</i>	[124]
	<i>Messerschmidia argentea</i>	[158]
7-Acetylechinatine	<i>Cynoglossum amabile</i>	[67]
	<i>Cynoglossum officinale</i>	[67,84]
	<i>Onosma erecta</i>	[69]
3'-Acetylechihumiline	<i>Onosma leptantha</i>	[166]
3'-Acetylechiumine	<i>Amsinckia menziessi</i> var. <i>intermedia</i>	[42]
	<i>Cryptantha clevelandii</i>	[63]
3'-Acetylechimidine	<i>Echium vulgare</i>	[96]
5'-Acetylechimidine	<i>Echium vulgare</i>	[11]
5'-Acetyleuropine	<i>Heliotropium disciforme</i>	[122]
	<i>Heliotropium rotundifolium</i>	[138]
7-Acetyleuropine	<i>Heliotropium bovi</i>	[110]
3'-Acetylfurcatine	<i>Amsinckia carinata</i>	[42]
	<i>Amsinckia furcata</i>	[42]
3'-Acetylheliosupine	<i>Cynoglossum creticum</i>	[70]
	<i>Cynoglossum officinale</i>	[67,83]
	<i>Heliotropium hirsutissimum</i>	[129]
7-Acetyl-9-(2-hydroxy-3-methylbutryl) retronecine	<i>Onosma arenaria</i>	[163]
3'-Acetyлиндicine	<i>Heliotropium arborescens</i> (<i>H. peruvianum</i>)	[28]
	<i>Messerschmidia argentea</i>	[158]
3'-Acetylintermedine	<i>Amsinckia eastwoodiae</i>	[42]
	<i>Amsinckia lycopsoides</i>	[42]
	<i>Amsinckia lycopsoides</i> × <i>menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[43]
	<i>Amsinckia retrosa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>microcarpa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>spectabilis</i>	[42]
	<i>Amsinckia tessellata</i>	[46]
	<i>Cryptantha cana</i>	[63]
	<i>Cryptantha crassipes</i>	[64]
	<i>Cryptantha clevelandii</i>	[63]
	<i>Cryptantha flava</i>	[63]
	<i>Cryptantha leiocarpa</i>	[63]
	<i>Cryptantha thyrsoflora</i>	[63]
	<i>Cryptantha virgata</i>	[63]
<i>Echium pininana</i>	[95]	

Table 2. Cont.

Compounds	Sources	References	
7-Acetylintermedine	<i>Amsinckia carinata</i>	[42]	
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]	
	<i>Amsinckia tessellata</i>	[46]	
	<i>Anchusa arvensis</i>	[40]	
	<i>Borago officinalis</i>	[55]	
	<i>Cryptantha cana</i>	[63]	
	<i>Cryptantha crassipes</i>	[64]	
	<i>Cryptantha flava</i>	[63]	
	<i>Cryptantha thyrsoflora</i>	[63]	
	<i>Cryptantha virgata</i>	[63]	
	<i>Lappula myostis</i>	[35]	
	<i>Lithospermum canescens</i>	[153,154]	
	<i>Onosma alborosea</i>	[161]	
	<i>Onosma arenaria pennina</i>	[161]	
	<i>Onosma stellulatum</i>	[167]	
	<i>Pulmonaria obscura</i>	[168]	
	<i>Symphytum officinale</i>	[171,172,179]	
	<i>Symphytum peregrinum</i>	[27]	
	<i>Symphytum</i> × <i>uplandicum</i>	[180]	
	5'-Acetylasiocarpine	<i>Heliotropium hirsutissimum</i>	[129]
7-Acetyl-9-latifolylretronecine	<i>Hackelia californica</i>	[101]	
3'-Acetyllithosenine	<i>Lithospermum officinale</i>	[156]	
3'-Acetylyllopsamine	<i>Amsinckia grandiflora</i>	[42]	
	<i>Amsinckia lunaris</i>	[42]	
	<i>Amsinckia menziesii</i>	[45]	
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]	
	<i>Amsinckia tessellata</i>	[46]	
	<i>Amsinckia tessellata</i> var. <i>tessellata</i>	[42]	
	<i>Cerinth glabra</i>	[40]	
	<i>Cryptantha cana</i>	[63]	
	<i>Cryptantha crassipes</i>	[64]	
	<i>Cryptantha flava</i>	[63]	
	<i>Cryptantha jamesii</i>	[66]	
	<i>Cryptantha thyrsoflora</i>	[63]	
	<i>Echium lycopsis</i> (<i>E. plantagineum</i>)	[93]	
	7-Acetylyllopsamine	<i>Amsinckia grandiflora</i>	[42]
		<i>Amsinckia menziesii</i>	[45]
		<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
		<i>Amsinckia tessellata</i>	[46]
<i>Amsinckia tessellate</i> var. <i>tessellata</i>		[42]	
<i>Anchusa arvensis</i>		[40]	
<i>Anchusa hispida</i>		[40]	
<i>Anchusa officinalis</i>		[48]	
<i>Borago officinalis</i>		[55]	
<i>Cerinth glabra</i>		[40]	

Table 2. Cont.

Compounds	Sources	References
7-Acetyllycopamine	<i>Cryptantha cana</i>	[63]
	<i>Cryptantha crassipes</i>	[64]
	<i>Cryptantha flava</i>	[63]
	<i>Cryptantha jamesii</i>	[66]
	<i>Cryptantha thyrsoflora</i>	[63]
	<i>Cryptantha virgata</i>	[63]
	<i>Echium horridum</i>	[90]
	<i>Echium hypertropicum</i>	[92]
	<i>Echium humile</i>	[91]
	<i>Echium rauwolfi</i>	[90]
	<i>Lappula myostis</i>	[35]
	<i>Lappula spinocarpos</i>	[40]
	<i>Lithospermum canesens</i>	[153,154]
	<i>Onosma alborosea</i>	[161]
	<i>Onosma arenaria</i>	[163]
	<i>Onosma arenaria pennina</i>	[161]
	<i>Pulmonaria obscura</i>	[168]
	<i>Symphytum bohemicum</i>	[173]
	<i>Symphytum officinale</i>	[171,172,179]
	<i>Symphytum peregrinum</i>	[27]
<i>Symphytum tanaicense</i>	[173]	
<i>Symphytum tubertosum</i>	[28]	
<i>Symphytum × uplandicum</i>	[180]	
7-Acetyl-9-(2-methylbutyryl) retronecine	<i>Onosma arenaria</i>	[163]
3'-Acetylmyscorpine	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia retrosa</i>	[42]
7-Acetylretronecine	<i>Onosma arenaria</i>	[163]
3'-Acetylriinderine	<i>Cynoglossum columnae</i>	[69]
	<i>Heliotropium transplinum</i>	[144]
7-Acetyl-9-sarracinoyl retronecine	<i>Alkanna tinctoria</i>	[40]
7-Acetylscorpioidine	<i>Myosotis scorpioides</i>	[159]
3'-Acetylsupinine	<i>Onosma arenaria</i>	[163]
3'-Acetyltessellatine	<i>Amsinckia tessellata</i> var. <i>tessellata</i>	[42]
9-Acetytessellatine	<i>Amsinckia grandifkora</i>	[42]
	<i>Amsinckia lunaris</i>	[42]
	<i>Amsinckia tessellata</i> var. <i>tessellata</i>	[42]
	<i>Heliotropium floridum</i>	[128]
3'-Acetyltrachelanthamine	<i>Anchusa arvensis</i>	[40]
9-Acetyltrachelanthamine	<i>Amsinckia tessellata</i> var. <i>gloriosa</i>	[42]
3'-Acetylviridiflorine	<i>Heliotropium curassavicum</i> var. <i>argentinum</i>	[119]
9-(3'-Acetyl)viridiflory retronecine	<i>Heliotropium curassavicum</i> var. <i>curassavicum</i>	[119]
	<i>A. douglasiana</i>	[42]
9-(3'-Acetylviridifloryl) turniforcidine	<i>A. tessellata</i> var. <i>tessellata</i>	[42]

Table 2. Cont.

Compounds	Sources	References
7-Acetylvulgarine	<i>Echium vulgare</i>	[11]
Amabiline	<i>Amsinckia douglasina</i>	[42]
	<i>Amsinckia eastwoodiae</i>	[42]
	<i>Amsinckia grandiflora</i>	[42]
	<i>Amsinckia lycopsoides</i>	[42]
	<i>Amsinckia lycopsodes menziesii</i>	[42]
	var. <i>intermedium</i>	
	<i>Amsinckia menziesii</i> var. <i>intermedium</i>	[42]
	<i>Amsinckia retrosa</i>	[42]
	<i>Amsinckia tessellata</i> var. <i>gloriosa</i>	[42]
	<i>Amsinckia tessellata</i> var. <i>tessellata</i> .	[42]
	<i>Asperugo procumbens</i>	[47]
	<i>Borago officinalis</i>	[55]
	<i>Cryptantha confertiflora</i>	[63]
	<i>Cryptantha crassipes</i>	[64]
	<i>Cryptantha virginensis</i>	[63]
	<i>Cynoglossum amabile</i>	[67,68]
	<i>Cynoglossum glochidiatum</i>	[78]
	<i>Heliotropium spathulatum</i>	[140]
	<i>Lappula spinocarpos</i>	[40]
	<i>Lindelofia angustiflora</i>	[78]
	<i>Neatostema apulum</i>	[160]
Anadoline	<i>Symphytum orientale</i>	[28]
	<i>Symphytum tuberosum</i>	[28]
7 α -Angeloyl-1-chloromethy-1,2-dihydropyrrolizidine	<i>Cynoglossum creticum</i>	[70]
7-Angeloyl-9-(2,3-dihydroxybutyryl)heliotridine	<i>Cynoglossum officinale</i>	[67]
7-Angeloyl-9-(2,3-dihydroxybutyryl)retronecine	<i>Echium horridum</i>	[90]
	<i>Echium rauwolfii</i>	[90]
	<i>Echium setosum</i>	[96]
	<i>Onosma arenaria</i>	[163]
7-Angeloyl-9-(2,3-dihydroxypropanoyl)retronecine	<i>Alkanna orientalis</i>	[40]
	<i>Alkanna tinctoria</i>	[40]
7-Angeloyl-1-formyl-6,7-dihydro-5H-pyrrolizidine	<i>Cynoglossum officinale</i>	[67]
7-Angeloyl-9-(hydroxypropenoyl)retronecine	<i>Alkanna orientalis</i>	[40]
	<i>Alkanna tinctoria</i>	[40]
7-Angeloylechinatine	<i>Cynoglossum officinale</i>	[67]
7-Angeloylheliotridine	<i>Anchusa hispida</i> (<i>Gastrocotyle hispida</i>)	[40]
	<i>Anchusa milleri</i>	[40]
	<i>Cynoglossum creticum</i>	[70,72]
	<i>Cynoglossum latifolium</i>	[79]
	<i>Cynoglossum officinale</i>	[67,84]
	<i>Heliotropium curassavicum</i>	[117]
	<i>Heliotropium supinum</i>	[27,143]
	<i>Lappula spinocarpos</i>	[40]

Table 2. Cont.

Compounds	Sources	References
7-Angeloylheliotridine	<i>Paracaryum intermedium</i>	[40]
	<i>Paracaryum regulosum</i>	[40]
	<i>Rindera austroechinata</i>	[57]
7-Angeloylheliotrine	<i>Heliotropium circinatum</i>	[114]
	<i>Heliotropium digynum</i> (<i>H. luteum</i>)	[121]
	<i>Heliotropium eichwaldii</i>	[124]
	<i>Heliotropium europaeum</i>	[127]
	<i>Rindera umbellata</i>	[169]
7-Angeloyllycopsamine	<i>Echium horridum</i>	[90]
	<i>Echium rauwolfii</i>	[90]
7-Angeloyl-9-(2-methylbutyryl)heliotridine	<i>Cynoglossum creticum</i>	[70]
	<i>Cynoglossum offocinale</i>	[67]
7-Angeloyl-9-(2-methylbutyryl)retronecine	<i>Echium horridum</i>	[90]
	<i>Echium rauwolfii</i>	[90]
7-Angeloylretronecine	<i>Alkanna orientalis</i>	[40,41]
	<i>Alkanna tinctoria</i> (<i>A. tuberculata</i>)	[40,184]
	<i>Arnebia decumbens</i>	[52]
	<i>Arnebia euchroma</i>	[53]
	<i>Cerintho minor</i>	[60]
	<i>Cryptantha fendleri</i>	[63]
	<i>Cryptantha leiocarpa</i>	[63]
	<i>Echium amoenum</i>	[87]
	<i>Echium glomeratum</i>	[89]
	<i>Echium horridum</i>	[90]
	<i>Echium rauwolfii</i>	[90]
	<i>Echium setosum</i>	[96]
	<i>Echium simplex</i>	[162]
	<i>Echium vulgare</i>	[96]
	<i>Eritrichium rupestre</i>	[60]
	<i>Hackelia longituba</i>	[104]
	<i>Heliotropium bursiferum</i>	[113]
	<i>Symphytum tuberosum</i>	[162]
	9-Angeloylretronecine	<i>Alkanna orientalis</i>
<i>Arnebia decumbens</i>		[52]
<i>Cryptantha fendleri</i>		[63]
<i>Cryptantha leiocarpa</i>		[63]
<i>Cynoglossum amabilie</i>		[67]
<i>Echium glomaratum</i>		[89]
<i>Echium hypertropicum</i>		[92]
<i>Echium setosum</i>		[96]
<i>Echium simplex</i>		[162]
<i>Echium vulgare</i>		[96]
<i>Hackelia longituba</i>		[104]
<i>Messerchimidia sibirica</i>		[28]
<i>Myosotis sylvatica</i>		[25]

Table 2. Cont.

Compounds	Sources	References
7-Angeloylrinderine	<i>Cynoglossum officinale</i>	[67]
9-Angeloyltrachelanthamidine	<i>Anchusa arvensis</i>	[40]
7-Angeloyl-9-(+)-trachelanthylheliotridine	<i>Rindera umbellata</i>	[169]
9-Angeloyl-7-iridiflorylretronecine	<i>Cerintho minor</i>	[60]
	<i>Cynoglossum amabile</i>	[60]
	<i>Cynoglossum clandestinum</i>	[60]
	<i>Echium tuberculatum</i>	[60]
	<i>Eritrichium rupestre</i>	[60]
	<i>Echium vulgare</i>	[98]
	<i>Symphytum asperum</i>	[172]
Asperumine	<i>Symphytum caucasicum</i>	[174]
	<i>Onosma arenaria</i>	[163]
9-(Butyryl-2-ene) supinidine	<i>Lithospermum canescens</i>	[153,154]
Canescine	<i>Lithospermum canescens</i>	[153,154]
Canescenine	<i>Lithospermum canescens</i>	[153,154]
Carategine	<i>Lindelofia tschimganica</i>	[27]
	<i>Rindera oblongifolia</i>	[152]
	<i>Solanthus karateginus</i>	[151]
	<i>Heliotropium curassavicum</i>	[117,118]
Coromandaline	<i>Heliotropium spathulatum</i>	[140]
	<i>Heliotropium curassavicum</i>	[117]
Coromandalinine	<i>Heliotropium spathulatum</i>	[140]
	<i>Heliotropium curassavicum</i>	[117]
Cryptanthine	<i>Cryptantha utahensis</i>	[65]
Curassanecine	<i>Heliotropium curassavicum</i>	[117]
Curassavine	<i>Anchusa officinalis</i>	[49]
	<i>Heliotropium curassavicum</i>	[117]
	<i>Heliotropium spathulatum</i>	[140]
	<i>Heliotropium curassavicum</i>	[117]
Curassavinine	<i>Heliotropium spathulatum</i>	[140]
	<i>Anchusa milleri</i>	[40]
9-Curassavorylheliotridine	<i>Cynoglossum australe</i>	[68]
Cynaustriine	<i>Cynoglossum lanceolatum</i>	[78]
	<i>Cynoglossum montanum</i>	[81]
	<i>Amsinckia douglasiana</i>	[42]
	<i>Cynoglossum australe</i>	[68]
	<i>Cynoglossum furcatum</i>	[73]
Cynaustriine	<i>Cynoglossum lanceolatum</i>	[78]
	<i>Cynoglossum montanum</i>	[81]
	<i>Cynoglossum creticum</i>	[72]
	<i>Heliotropium europaeum</i>	[185]
Cynoglossamine	<i>Heliotropium europaeum</i>	[185]
Dehydroheliotrine	<i>Heliotropium dissitiflorum</i>	[123]
5-Deoxylasiocarpine	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
3',7-Diacetylintermidine	<i>Amsinckia tessellata</i>	[46]
	<i>Anchusa arvensis</i>	[40]
	<i>Amsinckia menziesii</i>	[45]
3',7-Diacetylylcopsamine	<i>Amsinckia menziesii</i>	[45]
	<i>Amsinckia tessellata</i>	[46]

Table 2. Cont.

Compounds	Sources	References
3',7-Diacetyllycopsamine	<i>Anchusa arvensis</i>	[40]
	<i>Cerinth glabra</i>	[59]
3',9-Diacetyltessellate	<i>Amsinckia tessellata</i> var. <i>tessellata</i>	[42]
5,6-Dihydro-7,9-dimethoxy-7H-pyrrolizine	<i>Onosma arenaria</i>	[163]
Dihydroechinatine	<i>Onosma stellulatum</i>	[167]
<i>thero</i> -2",3"-Dihydroxyechiumine	<i>Cryptantha clevelandii</i>	[63,65]
	<i>Cryptantha inequata</i>	
	<i>Cryptantha leiocarpa</i>	[63]
Dihydroxytriangularine	<i>Alkanna orientalis</i>	[40,41]
	<i>Alkanna tinctoria</i>	[40,41]
Dihydroxytriangularicine	<i>Alkanna orientalis</i>	[40]
	<i>Alkanna tinctoria</i>	[40]
Echiumiline	<i>Echium hypertropicum</i>	[92]
	<i>Echium humile</i>	[91]
	<i>Echium vulgare</i>	[96]
	<i>Onosma leptantha</i>	[166]
Echimidine	<i>Arnebia hispidissima</i>	[54]
	<i>Cryptantha inequata</i>	[65]
	<i>Echium amoenum</i>	[87]
	<i>Echium angustifolium</i>	[88]
	<i>Echium horridum</i>	[90]
	<i>Echium humile</i>	[91]
	<i>Echium hypertropicum</i>	[92]
	<i>Echium italicum</i>	[28]
	<i>Echium lycopsis</i> (<i>E. plantagineum</i>)	[94]
	<i>Echium pininana</i>	[95]
	<i>Echium rauwolfii</i>	[90]
	<i>Echium sericeum</i>	[54]
	<i>Echium. setosum</i>	[96]
	<i>Echium stenosphon</i> subsp. <i>stenosphon</i>	[92]
	<i>Echium tuberculatum</i>	[60]
	<i>Echium vulgare</i>	[11,96]
	<i>Echium wildpretii</i>	[99]
	<i>Onosma stellulatum</i>	[60,167]
	<i>Symphytum aintabicum</i>	[170]
	<i>Symphytum asperum</i>	[171]
<i>Symphytum bohemicum</i>	[173]	
<i>Symphytum caucasicum</i>	[174]	
<i>Symphytum consolidum</i>	[175]	
<i>Symphytum sylvaticum</i>	[170]	
<i>Symphytum tuberosum</i>	[162]	
Echimidine isomer (tigloyl)	<i>Echium amoenum</i>	[87]
	<i>Echium horridum</i>	[90]

Table 2. Cont.

Compounds	Sources	References
Echimidine isomer (tigloyl)	<i>Echium rauwolfii</i>	[90]
	<i>Echium setosum</i>	[96]
	<i>Echium vulgare</i>	[96]
Echimiplatine	<i>Cryptantha crassipes</i>	[64]
	<i>Echium plantagineum</i>	[93]
	<i>Echium vulgare</i>	[11]
Echinatine	<i>Asperugo procumbens</i>	[47]
	<i>Cynoglossum amabile</i>	[67,68]
	<i>Cynoglossum columnae</i>	[69]
	<i>Cynoglossum creticum</i>	[70–72]
	<i>Cynoglossum furcatum</i> (<i>C. zeylanicum</i>)	[74,75]
	<i>Cynoglossum germanicum</i>	[77]
	<i>Cynoglossum macrostylum</i>	[80]
	<i>Cynoglossum montanum</i>	[81]
	<i>Cynoglossum nervosum</i>	[82]
	<i>Cynoglossum officinale</i>	[67,84]
	<i>Cynoglossum pictum</i>	[85]
	<i>Heliotropium circinatum</i>	[114]
	<i>Heliotropium indicum</i>	[130]
	<i>Heliotropium suaveolens</i>	[29]
	<i>Heliotropium supinum</i>	[27,143]
	<i>Lappula glochidiata</i>	[146]
	<i>Lindelofia longiflora</i>	[149]
	<i>Lindelofia spectabilis</i>	[124]
	<i>Lindelofia stylosa</i>	[135]
	<i>Moltikiopsis ciliata</i>	[108]
	<i>Paracaryum regulosum</i>	[40]
	<i>Paracynoglossum imeretium</i>	[29]
	<i>Rindera austroechinata</i>	[57,152]
	<i>Rindera baldschuanica</i>	[152]
	<i>Rindera cyclodonata</i>	[120]
	<i>Rindera echinata</i>	[120]
<i>Rindera oblogifolia</i>	[152]	
<i>Rindera umbellata</i>	[169]	
<i>Solenanthus circinnatus</i>	[151]	
<i>Solenanthus coronatus</i>	[135]	
<i>Solenanthus karateginus</i>	[151]	
<i>Symphytum asperum</i>	[172]	
<i>Symphytum caucasicum</i>	[174]	
<i>Symphytum officinale</i>	[179]	
<i>Tournefortia sogdiana</i>	[57]	
Echiumine	<i>Amsinckia carinata</i>	[42]
	<i>Amsinckia eastwoodiae</i>	[42]
	<i>Amsinckia hispida</i>	[44]
	<i>Amsinckia intermedia</i>	[44]

Table 2. Cont.

Compounds	Sources	References
Echiumine	<i>Amsinckia lycopsoides</i>	[44]
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
	<i>Cryptantha clevelandii</i>	[63]
	<i>Cryptantha crassipes</i>	[64]
	<i>Cryptantha leiocarpa</i>	[63]
	<i>Echium lycopsis</i>	[94]
Echiupine	<i>Echium pininana</i>	[95]
Echiuplatine	<i>Cryptantha inequata</i>	[65]
	<i>Echium plantagineum</i>	[93]
	<i>Echium vulgare</i>	[11]
Echivulgarine	<i>Echium vulgare</i>	[11]
Ehretinine	<i>Ehretia aspera</i>	[100]
2",3"-Epoxyechiumine	<i>Cryptantha clevelandii</i>	[63]
	<i>Cryptantha leiocarpa</i>	[63]
<i>Erythro</i> -2",3"-chloro-2"-hydroxyechiumine	<i>Cryptantha clevelandii</i>	[63]
	<i>Cryptantha leiocarpa</i>	[63]
7-Epi-echimiplatine	<i>Onosma erecta</i>	[69]
1 α -2 α -Epoxy-1 β -hydroxymethyl-8 α -pyrrolizidine	<i>Heliotropium transalpinum</i> var. <i>transalpinum</i>	[145]
	<i>Heliotropium arbainense</i>	[71]
Europine	<i>Heliotropium bacciferum</i>	[108,109]
	<i>Heliotropium bovi</i>	[110]
	<i>Heliotropium circinatum</i>	[114]
	<i>Heliotropium crassifolium</i>	[115]
	<i>Heliotropium digynum</i> (<i>H.luteum</i>)	[121]
	<i>Heliotropium dissitiflorum</i>	[123]
	<i>Heliotropium esfandiarii</i>	[125]
	<i>Heliotropium europaeum</i>	[126,127,186]
	<i>Heliotropium hirsutissimum</i>	[129]
	<i>Heliotropium marifolium</i>	[29]
	<i>Heliotropium maris mortui</i>	[71]
<i>Heliotropium rotundifolium</i>	[137,138]	
Floridanine	<i>Cordia sinensis</i>	[62]
Floridimine	<i>Heliotropium floridum</i>	[128]
Floridine	<i>Heliotropium floridum</i>	[128]
Floridinine	<i>Heliotropium floridum</i>	[128]
Furcatine	<i>Amsinckia carinata</i>	[42]
	<i>Amsinckia furacata</i>	[42]
	<i>Amsinckia vernicosa</i>	[42]
Hackelidine	<i>Hackelia californica</i>	[102]
Heleurine	<i>Heliotropium bacciferum</i>	[109]
	<i>Heliotropium circinatum</i>	[114]
	<i>Heliotropium disciforme</i>	[122]
	<i>Heliotropium europaeum</i>	[126,127,186]
	<i>Heliotropium hirsutissimum</i>	[129]
	<i>Heliotropium indicum</i>	[131]

Table 2. Cont.

Compounds	Sources	References
Helibracteatine	<i>Heliotropium bracteatum</i>	[112]
Helibractinecine	<i>Heliotropium bracteatum</i>	[111]
Helibracteatinecine	<i>Heliotropium bracteatum</i>	[112]
Helibracteatinine	<i>Heliotropium bracteatum</i>	[112]
Heliofoline	<i>Heliotropium ovalifolium</i>	[136]
Helindicine	<i>Heliotropium indicum</i>	[130]
Heliocoromandaline	<i>Heliotropium curassavicum</i>	[117]
Heliocurassavine	<i>Heliotropium curassavicum</i>	[117]
Heliocurassavicine	<i>Heliotropium curassavicum</i>	[117]
Heliocurassavinine	<i>Heliotropium curassavicum</i>	[117]
Heliospathine	<i>Heliotropium spathulatum</i>	[140]
Heliospathuline	<i>Heliotropium spathulatum</i>	[140]
	<i>Onosma stellulatum</i>	[167]
Heliosupine	<i>Cynoglossium creticum</i>	[70–72]
	<i>Cynoglossium macrostylum</i>	[80]
	<i>Cynoglossium montatum</i>	[81]
	<i>Cynoglossium officinale</i>	[67,83,84]
	<i>Cynoglossium pictum</i>	[85]
	<i>Cynoglossium viridiforum</i>	[86]
	<i>Heliotropium supinum</i>	[27,143]
	<i>Myosotis sylvatica</i>	[25]
	<i>Paracaryum regulosum</i>	[90]
	<i>Paracynoglossum imeretium</i>	[29]
	<i>Rindera umbellata</i>	[169]
	<i>Symphytum asperum</i>	[171]
	<i>Symphytum officinale</i>	[179]
Heliotridine	<i>Anchusa milleri</i>	[90]
	<i>Onosma heterophyllum</i>	[165]
Heliotridine 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester	<i>Anchusa strigosa</i>	[50]
Heliotrine	<i>Arenbia decumbens</i>	[52]
	<i>Cynoglossum nervosum</i>	[82]
	<i>Heliotropium acutifolium</i>	[105]
	<i>H. arbainense</i>	[71]
	<i>H. bacciferum</i>	[108,109]
	<i>Heliotropium circinatum</i>	[114]
	<i>Heliotropium dasycarpum</i>	[120]
	<i>Heliotropium digynum</i>	[121]
	<i>Heliotropium disciforme</i>	[122]
	<i>Heliotropium dissitiflorum</i>	[123]
	<i>Heliotropium eichwaldii</i>	[124]
	<i>Heliotropium europaeum</i>	[127,185,186]
	<i>Heliotropium hirsutissimum</i>	[129]
	<i>Heliotropium indicum</i>	[130,131]
	<i>Heliotropium lasiocarpum</i>	[29]

Table 2. Cont.

Compounds	Sources	References
Heliotrine	<i>Heliotropium marifolium</i>	[29]
	<i>Heliotropium olgae</i>	[135]
	<i>Heliotropium popovii</i> subsp. <i>gillianum</i>	[28]
	<i>Heliotropium rotundifolium</i>	[137,138]
	<i>Heliotropium suaveolens</i>	[29]
	<i>Heliotropium supinum</i>	[27,143]
	<i>Heliotropium transoxanum</i>	[27]
	<i>Molyikiopsis ciliate</i> (<i>Lithospermum callosum</i>)	[108]
	<i>Symphytum caucasicum</i>	[174]
Heliovicine	<i>Heliotropium spathulatum</i>	[140]
Heliscabine	<i>Heliotropium scabrum</i>	[139]
Hydroxymyoscorpine	<i>Echium pininana</i>	[95]
Ilamine	<i>Heliotropium crassifolium</i>	[115]
Incanine	<i>Heliotropium olgae</i>	[29]
	<i>Trichodesma incanum</i>	[46]
Indicine	<i>Heliotropium amplexicaule</i>	[29]
	<i>Heliotropium arborescens</i> (<i>H. pruvianum</i>)	[107]
	<i>Heliotropium indicum</i>	[130,131]
	<i>Heliotropium marifolium</i>	[29]
	<i>Heliotropium transalpinum</i>	[144]
	<i>Messerschmidia argentea</i>	[158]
Indicinine	<i>Heliotropium indicum</i>	[130,131]
Isoechinatine	<i>Cynoglossum furcatum</i> (<i>C. zeylanicum</i>)	[75]
Isolycopsamine	<i>Heliotropium keralense</i>	[190]
Isoretronocanol (or its isomer)	<i>Omphalodes verna</i>	[27]
9-(3'-Isovaleryl)viridiflory retronecine	<i>Heliotropium curassavicum</i> var. <i>argentinum</i>	[119]
	<i>Heliotropium curassavicum</i> var. <i>curassavicum</i>	[119]
	<i>Amsinckia carinata</i>	[42]
Intermedine	<i>Amsinckia douglasiana</i>	[42]
	<i>Amsinckia eastwoodiae</i>	[42]
	<i>Amsinckia furcata</i>	[42]
	<i>Amsinckia grandiflora</i>	[42]
	<i>Amsinckia hispida</i>	[44]
	<i>Amsinckia intermedia</i>	[44]
	<i>Amsinckia lunaris</i>	[42]
	<i>Amsinckia lycopsoides</i>	[42,44]
	<i>Amsinckia lycopsoides</i> × <i>menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia menziesii</i>	[45]
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia retrosa</i>	[42]

Table 2. Cont.

Compounds	Sources	References
Intermedine	<i>Amsinckia spectabilis</i> var. <i>microcarpa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>spectabilis</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>nicolai</i>	[42]
	<i>Amsinckia tessellata</i>	[46]
	<i>Amsinckia tessellata</i> var. <i>gloriosa</i>	[42]
	<i>Amsinckia tessellata</i> var. <i>tessellata</i>	[42]
	<i>Amsinckia vernicosa</i>	[42]
	<i>Anchusa arvensis</i> (<i>Lycopsis arvensis</i>)	[40]
	<i>Anchusa hispidia</i> (<i>Gastrocotyle hispidia</i>)	[40]
	<i>Anchusa officinalis</i>	[48]
	<i>Borago officinalis</i>	[55]
	<i>Cerintho minor</i>	[61]
	<i>Cryptantha cana</i>	[63]
	<i>Cryptantha clevelandii</i>	[63]
	<i>Cryptantha confertiflora</i>	[63]
	<i>Cryptantha flava</i>	[63]
	<i>Cryptantha inequata</i>	[65]
	<i>Cryptantha jamesii</i>	[66]
	<i>Cryptantha leiocarpa</i>	[63]
	<i>Cryptantha thyrsoflora</i>	[63]
	<i>Cryptantha virgata</i>	[63]
	<i>Cryptantha virginiana</i>	[63]
	<i>Heliotropium keralense</i>	[133]
	<i>Heliotropium transalpinum</i>	[144]
	<i>Lappula myostis</i>	[35]
	<i>Lappula spinocarpas</i>	[40]
	<i>Lithospermum erythrorhizon</i>	[155]
	<i>Mertensia ciliate</i>	[157]
	<i>Onosma alborosea</i>	[161]
	<i>Onosma arenaria pennina</i>	[161]
	<i>Pulmonaria obscura</i>	[168]
	<i>Symphytum peregrinum</i>	[27]
	<i>Symphytum</i> × <i>uplandicum</i>	[180]
<i>Trichodesma africanum</i>	[71]	
Lactodine	<i>Cynoglossum furcatum</i>	[76,187]
Lasiocarpine	<i>Heliotropium arbainense</i>	[71]
	<i>Heliotropium bovei</i>	[110]
	<i>Heliotropium circinatum</i>	[114]
	<i>Heliotropium digynum</i>	[121]
	<i>Heliotropium eichwaldii</i>	[124]
	<i>Heliotropium europaeum</i>	[126,127,186]
	<i>Heliotropium hirsutissimum</i>	[129]
	<i>Heliotropium indicum</i>	[130,131]
<i>Heliotropium lasiocarpum</i>	[29]	
<i>Heliotropium marifolium</i>	[29]	

Table 2. Cont.

Compounds	Sources	References
Lasiocarpine	<i>Heliotropium maris mortui</i>	[137]
	<i>Heliotropium rotundifolium</i>	[137,138]
	<i>Heliotropium suaveolens</i>	[29]
	<i>Lappula intrmedia</i>	[27]
	<i>Symphytum caucasicum</i>	[174]
	<i>Symphytum officinale</i>	[177]
Latifoline	<i>Cryptantha fendleri</i>	[63]
	<i>Cynoglossum latifolium</i>	[79]
	<i>Hackelia californica</i>	[101]
	<i>Hackelia floribunda</i>	[103]
	<i>Hackelia longituba</i>	[104]
	<i>Lindelofia stylosa</i>	[27]
9-Latifolyltretronecine	<i>Hackelia californica</i>	[101]
Leptanthine	<i>Cryptantha crassipes</i>	[64]
	<i>Echium plantagineum</i>	[93]
	<i>Echium vulgare</i>	[11]
	<i>Onosma leptantha</i>	[166]
	<i>Onosma stellulatum</i>	[167]
Lindelofine	<i>Amsickia menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsickia spectabilis</i> var. <i>microcarpa</i>	[42]
	<i>Amsickia spectabilis</i> var. <i>spectabilis</i>	[42]
	<i>Amsickia spectabilis</i> var. <i>nicola</i>	[42]
	<i>Lindelofia anchusoides</i> (L. <i>macrostyle</i>)	[28]
	<i>Rindera umbellata</i>	[169]
Lindelofamine	<i>Lindelofia anchusoides</i> (L. <i>macrostyle</i>)	[28]
Lindelofidine	<i>Heliotropium angiospermum</i>	[106]
	<i>Heliotropium confertifolium</i>	[106]
	<i>Heliotropium curassavicum</i>	[106]
	<i>Heliotropium foliosissimum</i>	[106]
	<i>Heliotropium fruticosum</i>	[106]
	<i>Heliotropium gregii</i>	[106]
	<i>Heliotropium indicum</i>	[106,116]
	<i>Heliotropium molle</i>	[106]
	<i>Heliotropium procumbens</i>	[106]
	<i>Heliotropium queretaroanum</i>	[106]
	<i>Heliotropium spathulatum</i>	[116]
	<i>Heliotropium sessei</i>	[106]
	<i>Heliotropium racemosum</i>	[106]
	<i>Heliotropium ternatum</i>	[106]
	<i>Heliotropium wigginsii</i>	[106]
Lithosenine	<i>Lithospermum officinale</i>	[156]
Longitubine	<i>Hackelia californica</i>	[101]
	<i>Hackelia logituba</i>	[104]
Lycopsamine	<i>Amsinckia carinata</i>	[42]
	<i>Amsinckia douglasiana</i>	[42]

Table 2. Cont.

Compounds	Sources	References
Lycopsamine	<i>Amsinckia eastwoodiae</i>	[42]
	<i>Amsinckia furcata</i>	[42]
	<i>Amsinckia grandiflora</i>	[42]
	<i>Amsinckia hispida</i>	[44]
	<i>Amsinckia intermedia</i>	[44]
	<i>Amsinckia lunaris</i>	[42]
	<i>Amsinckia lycopsoides</i>	[42,44]
	<i>Amsinckia lycopsoides</i> × <i>menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia menziesii</i>	[45]
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia retrosa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>microcarpa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>spectabilis</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>nicolai</i>	[42]
	<i>Amsinckia tessellata</i>	[46]
	<i>Amsinckia tessellata</i> var. <i>gloriosa</i>	[42]
	<i>Amsinckia tessellata</i> var. <i>tessellata</i>	[42]
	<i>Amsinckia vernicosa</i>	[42]
	<i>Anchusa arvensis</i> (<i>Lycopsis arvensis</i>)	[40]
	<i>Anchusa hispida</i> (<i>Gastrocotyle hispida</i>)	[40]
	<i>Anchusa officinalis</i>	[48]
	<i>Arnebia decumbens</i>	[52]
	<i>Borago officinalis</i>	[55]
	<i>Cerinthe glabra</i>	[59]
	<i>Cerinthe minor</i>	[61]
	<i>Cryptantha cana</i>	[63]
	<i>Cryptantha confertiflora</i>	[63]
	<i>Cryptantha flava</i>	[63]
	<i>Cryptantha inequata</i>	[65]
	<i>Cryptantha jamesii</i>	[66]
	<i>Cryptantha thyrsoflora</i>	[63]
	<i>Cryptantha virgata</i>	[63]
	<i>Cryptantha virginiana</i>	[63]
	<i>Cynoglossum amabile</i>	[67]
	<i>Echium hypertropicum</i>	[92]
	<i>Heliotropium transalpinum</i>	[144]
	<i>Heliotropium megalanthum</i>	[134]
	<i>Heliotropium steudneri</i>	[27]
	<i>Lappula myostis</i>	[35]
	<i>Lappula spinocarpas</i>	[40]
<i>Lithospermum purpureoeruleum</i>	[60]	

Table 2. Cont.

Compounds	Sources	References
Lycopsamine	<i>Mertensia bakeri</i>	[157]
	<i>Mertensia ciliate</i>	[157]
	<i>Mertensia sibirica</i>	[28]
	<i>Neatostema apulum</i>	[60]
	<i>Onosma alborosea</i>	[161]
	<i>Onosma arenaria pennina</i>	[161]
	<i>Onosma stellulatum</i>	[167]
	<i>Pulmonaria obscura</i>	[168]
	<i>Symphytum bohemicum</i>	[173]
	<i>Symphytum grandiflorum</i>	[176]
	<i>Symphytum ibericum</i>	[176]
	<i>Symphytum peregrinum</i>	[27]
	<i>Symphytum officinale</i>	[171,177]
	<i>Symphytum tanaicense</i>	[173]
	<i>Symphytum tuberosum</i>	[162,176]
	<i>Symphytum</i> × <i>uplandicum</i>	[180]
<i>Trichodesma africanum</i>	[71]	
Macrophylline	<i>Cordia myxa</i>	[62]
Macrotamine	<i>Macrotomia echioides</i>	[28]
Megalanthonine	<i>Heliotropium megalanthum</i>	[134]
Methyechiuplatine	<i>Cryptantha inequata</i>	[65]
1-Methylene-8 α -pyrrolizidine	<i>Onosma heterophyllum</i>	[165]
7-(2-Methylbutyryl)retronecine	<i>Echium humile</i>	[91]
	<i>Echium vulgare</i>	[96]
9-(2-Methylbutyryl)retronecine	<i>Echium vulgare</i>	[96]
7-(2-Methylbutyryl)-9-(2,3-dihydroxybutyryl)retronecine	<i>Echium humile</i>	[91]
	<i>Echium vulgare</i>	[96]
7-(2-Methylbutyryl)-9-echimidinyl retronecine	<i>Echium humile</i>	[91]
	<i>Echium hypertropicum</i>	[92]
	<i>Echium stenosphon</i> subsp. <i>stenosphon</i>	[92]
	<i>Echium vulgare</i>	[96]
Monocrotaline	<i>Arnebia hispidissima</i>	[54]
	<i>Lindelofia spectabilis</i>	[124]
Myoscorpine	<i>Amsinckia carinata</i>	[42]
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia retrosa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>microcarpa</i>	[42]
	<i>Echium pininana</i>	[95]
	<i>Linelfolia erythrorhizon</i>	[155]
	<i>Myosotis scorpioides</i>	[159]
Neocoromandaline	<i>Cynoglossum furcatum</i>	[74]
Neolatifoline	<i>Cryptantha fendleri</i>	[63]
	<i>Hackelia logituba</i>	[104]
Onosmectine	<i>Onosma erecta</i>	[69]

Table 2. Cont.

Compounds	Sources	References
(7 <i>S</i> ,8 <i>R</i>)Petranine	<i>Echium glomeratum</i>	[89]
(7 <i>S</i> ,8 <i>S</i>)Petranine	<i>Echium glomeratum</i>	[89]
Pictumine	<i>Cynoglossum pictum</i>	[28]
Platynecine	<i>Cryptantha leiocarpa</i>	[63]
Platynecine <i>N</i> -oxide 2 <i>S</i> -hydroxy-2 <i>S</i> (1 <i>S</i> -hydroxyethyl)-4-methyl-pentanosyl ester	<i>Anchusa strigosa</i>	[50,51]
Punctanecine	<i>Rindera umbellata</i>	[169]
Pycnanthine	<i>Echium humile</i>	[91]
Retronecine	<i>Anchusa hispida</i> (<i>Gastrocotyle hispida</i>)	[40]
	<i>Echium vulgare</i>	[96]
	<i>Heliotropium angiospermum</i>	[106]
	<i>Heliotropium confertifolium</i>	[106]
	<i>Heliotropium curassavicum</i>	[106,116]
	<i>Heliotropium foliosissimum</i>	[106]
	<i>Heliotropium fruticosum</i>	[106]
	<i>Heliotropium gregii</i>	[106]
	<i>Heliotropium indicum</i>	[106,116]
	<i>Heliotropium keralense</i>	[133]
	<i>Heliotropium molle</i>	[106]
	<i>Heliotropium ovalifolium</i>	[136]
	<i>Heliotropium procumbens</i>	[106]
	<i>Heliotropium queretaroanum</i>	[106]
	<i>Heliotropium racemosum</i>	[106]
	<i>Heliotropium scabrum</i>	[139]
	<i>Heliotropium spathulatum</i>	[106,116]
	<i>Heliotropium sessei</i>	[106]
	<i>Heliotropium ternatum</i>	[106]
	<i>Heliotropium wigginsii</i>	[106]
	<i>Lappula spinocarpos</i>	[40]
	<i>Trichodesma africanum</i>	[40]
Retronecine-7:9- dibenzoate	<i>Caccinea glauca</i>	[58]
Retronecine 2 <i>S</i> -hydroxy-2 <i>S</i> (1 <i>S</i> -hydroxyethyl)-4-methyl-pentanosyl ester	<i>Anchusa strigosa</i>	[50,51]
Retronecine 2 <i>S</i> -hydroxy-2 <i>S</i> (1 <i>R</i> -hydroxyethyl)-4-methyl-pentanosyl ester	<i>Anchusa strigosa</i>	[50,51]
Rinderine	<i>Anchusa milleri</i>	[40]
	<i>Arnebia decumbens</i>	[52]
	<i>Cynoglossum columnae</i>	[69]
	<i>Cynoglossum creticum</i>	[70,72]
	<i>Cynoglossum officinale</i>	[67,84]
	<i>Heliotropium indicum</i>	[130,131]
	<i>Heliotropium peruvianum</i>	[29]
	<i>Heliotropium transalpinum</i>	[144]
	<i>Paracaryum intermedium</i>	[40]
	<i>Paracaryum regulosum</i>	[40]

Table 2. Cont.

Compounds	Sources	References
Rinderine	<i>Rindera austroechinata</i>	[57]
	<i>Rindera baldschuanica</i>	[152]
	<i>Solanthus turkestanicus</i>	[150]
Scorpioidine	<i>Myosotis scorpioides</i>	[159]
7-Senecioidhelotridine	<i>Cynoglossum creticum</i>	[70]
	<i>Paracarum intermedium</i>	[40]
7-Senecioidretronecine	<i>Alkanna orientalis</i>	[40]
	<i>Echium hypertropicum</i>	[92]
	<i>Echium humile</i>	[91]
9-Senecioidretronecine	<i>Alkanna orientalis</i>	[40]
	<i>Echium humile</i>	[91]
7-Senecioidrinderine	<i>Paracaryum intermedium</i>	[40]
7-Senecioidlycopsamine	<i>Echium humile</i>	[91]
Sincamidine	<i>Amsinckia intermedia</i>	[44]
Senkirikine	<i>Trichodesma ehrenbergii</i>	[54]
Strigosine	<i>Heliotopium strigosum</i>	[25,141]
Subulacine	<i>Heliotopium angiospermum</i>	[29]
	<i>Heliotopium molle</i>	[29]
	<i>Heliotopium subulacatum</i>	[29]
	<i>Heliotopium ternatum</i>	[27]
	<i>Heliotopium transalpinum</i> var. <i>transalpinum</i>	[145]
Supinine	<i>Amsinckia carinata</i>	[42]
	<i>Amsinckia eastwoodiae</i>	[42]
	<i>Amsinckia furcata</i>	[42]
	<i>Amsinckia lunaris</i>	[42]
	<i>Amsinckia lycopsoides</i>	[42,44]
	<i>Amsinckia lycopsoides</i> × <i>menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia retrosa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>microcarpa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>spectabilis</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>nicolai</i>	[42]
	<i>Amsinckia tessellate</i> var. <i>gloriosa</i>	[42]
	<i>Amsinckia tessellate</i> var. <i>tessellate</i>	[42]
	<i>Anchusa arvensis</i> (<i>Lycopsis arvensis</i>)	[40]
	<i>Anchusa melleri</i>	[40]
	<i>Arnebia decumbens</i>	[52]
	<i>Borago officinalis</i>	[55]
<i>Caccina crassifolia</i>	[57]	
<i>Cerinthe glabra</i>	[59]	
<i>Cynoglossum amabile</i>	[67]	
<i>Cynoglossum creticum</i>	[70]	

Table 2. Cont.

Compounds	Sources	References
Supinine	<i>Heliotropium bacciferum</i>	[109]
	<i>Heliotropium europaeum</i>	[127]
	<i>Heliotropium hirsutissimum</i>	[129]
	<i>Heliotropium indicum</i>	[130,131]
	<i>Heliotropium supinum</i>	[27,143]
	<i>Heliotropium transalpinum</i>	[144]
	<i>Lappula spinocarpos</i>	[40]
	<i>Tournefortia samentosa</i>	[28]
	<i>Trichodesma ehrenbergii</i>	[54]
	<i>Trichodesma zeylanicum</i>	[182]
Supinidine	<i>Heliotropium angiospermum</i>	[106]
	<i>Heliotropium confertifolium</i>	[106]
	<i>Heliotropium curassavicum</i>	[106,116]
	<i>Heliotropium foliosissimum</i>	[106]
	<i>Heliotropium fruticosum</i>	[106]
	<i>Heliotropium gregii</i>	[106]
	<i>Heliotropium indicum</i>	[106,116]
	<i>Heliotropium molle</i>	[106]
	<i>Heliotropium procumbens</i>	[106]
	<i>Heliotropium queretaroanum</i>	[106]
	<i>Heliotropium racemosum</i>	[106]
	<i>Heliotropium spathulatum</i>	[106,116]
	<i>Heliotropium sessei</i>	[106]
	<i>Heliotropium wigginsii</i>	[106]
Supinidine N-oxide 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester	<i>Anchusa strigosa</i>	[50,51]
Symlandine	<i>Amsinckia menziesii</i> var. <i>inermedia</i>	[42]
	<i>Echium sericeum</i>	[54]
	<i>Symphytum</i> × <i>uplandicum</i>	[180]
Symphytine	<i>Myosotis scorpioides</i>	[159]
	<i>Symphytum asperum</i>	[171]
	<i>Symphytum bohemicum</i>	[173]
	<i>Symphytum consolidum</i>	[175]
	<i>Symphytum grandiflorum</i>	[176]
	<i>Symphytum ibericum</i>	[176]
	<i>Symphytum officinale</i>	[171,177–179]
	<i>Symphytum orientale</i>	[28]
	<i>Symphytum peregrinum</i>	[27]
	<i>Symphytum tanaiense</i>	[173]
	<i>Symphytum tuberosum</i>	[28,176]
	<i>Symphytum</i> × <i>uplandicum</i>	[180]
Symviridine	<i>Symphytum asperum</i>	[172]
	<i>Symphytum officinale</i>	[172,177]
	<i>Symphytum</i> × <i>uplandicum</i>	[172]

Table 2. Cont.

Compounds	Sources	References
Tessellate	<i>Amsinckia douglasiana</i>	[42]
	<i>Amsinckia eastwoodiae</i>	[42]
	<i>Amsinckia furcata</i>	[42]
	<i>Amsinckia grandiflora</i>	[42]
	<i>Amsinckia lunaris</i>	[42]
	<i>Amsinckia lycopsoides</i>	[42,44]
	<i>Amsinckia lycopsoides</i> × <i>menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia menziesii</i> var. <i>intermedia</i>	[42]
	<i>Amsinckia retrosa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>microcarpa</i>	[42]
	<i>Amsinckia spectabilis</i> var. <i>nicolai</i>	[42]
	<i>Amsinckia tessellate</i> var. <i>gloriosa</i>	[42]
	<i>Amsinckia tessellate</i> var. <i>tessellate</i>	[42]
	<i>Cryptantha confertiflora</i>	[63]
	<i>Cryptantha virginiensis</i>	[63]
Thesinine	<i>Borago officinalis</i>	[56]
Thesinine-4'-O-β-D-glucoside	<i>Borago officinalis</i>	[56]
7-Tigloyl-9-(2-deoxy-2-methyl)echimidinyliheliotridinEchium	<i>Cynoglossum columnae</i>	[69]
7-Tigloyl-9-(2,3-dihydroxybutyryl)retronecine	<i>Echium horridum</i>	[90]
	<i>Echium rauwolfii</i>	[90]
	<i>Echium setosum</i>	[96]
	<i>Echium vulgare</i>	[96]
7-Tigloyl-9-(2,3-dihydroxypropanoyl)retronecine	<i>Alkanna orientalis</i>	[40]
	<i>Alkanna tincotora</i>	[40]
7-Tigloylheliotridine	<i>Cynoglossum officinale</i>	[67]
7-Tigloyllycopsamine	<i>Echium horridum</i>	[90]
	<i>Echium rauwolfii</i>	[90]
7-Tigloyl-9-(2-methylbutyryl)retronecine	<i>Echium horridum</i>	[90]
	<i>Echium rauwolfii</i>	[90]
	<i>Echium setosum</i>	[96]
	<i>Echium vulgare</i>	[96]
7-Tigloylretronecine	<i>Alkanna tinctoria</i>	[40]
	<i>Arnebia decumbens</i>	[40]
	<i>Echium amoenum</i>	[87]
	<i>Echium setosum</i>	[96]
	<i>Echium vulgare</i>	[96]
9-Tigloylretronecine	<i>Alkanna orientalis</i>	[40]
	<i>Alkanna tincotora</i>	[40]
	<i>Arnebia decumbens</i>	[52]
	<i>Echium horridum</i>	[90]
	<i>Echium rauwolfii</i>	[90]
	<i>Echium setosum</i>	[96]
	<i>Echium vulgare</i>	[96]

Table 2. Cont.

Compounds	Sources	References
Trachelanthamidine	<i>Heliotropium angiospermum</i>	[106]
	<i>Heliotropium confertifolium</i>	[106]
	<i>Heliotropium curassavicum</i>	[106,116,118]
	<i>Heliotropium foliosissimum</i>	[106]
	<i>Heliotropium fruticosum</i>	[106]
	<i>Heliotropium gregii</i>	[106]
	<i>Heliotropium indicum</i>	[106,116]
	<i>Heliotropium molle</i>	[106]
	<i>Heliotropium procumbens</i>	[106]
	<i>Heliotropium queretaroanum</i>	[106]
	<i>Heliotropium racemosum</i>	[106]
	<i>Heliotropium sessei</i>	[106]
	<i>Heliotropium spathulatum</i>	[106,116]
	<i>Heliotropium strigosa</i>	[25]
<i>Heliotropium wigginsii</i>	[106]	
Trachelanthamine	<i>Anchusa hispida</i>	[40]
	<i>Cynoglossum clandestinum</i>	[60]
	<i>Cynoglossum creticum</i>	[70]
	<i>Cynoglossum officinale</i>	[67]
	<i>Lappula spinocarpos</i>	[40]
	<i>Myosotis sylvatica</i>	[25]
	<i>Onosma stellulatum</i>	[167]
	<i>Rindera balaschuanica</i>	[152]
	<i>R. echinata</i>	[120]
	<i>Trachelanthus hissaricus</i>	[29]
	<i>Trachelanthus korolkovii</i>	[57,150]
Trachelanthine	<i>Trachelanthus hissaricus</i>	[29]
	<i>Trachelanthus korolkovii</i>	[150]
7-Trachelanthyl-laburnine	<i>Rindera umbellata</i>	[169]
7-Trachelanthylretronecine	<i>Amsinckia vernicosa</i>	[42]
Transalpinecine	<i>Heliotropium transalpinum</i> var.	[145]
	<i>transalpinum</i>	
Triangularine	<i>Alkanna orientalis</i>	[40]
	<i>Alkanna tinctoria</i>	[40]
Triangularicine	<i>Alkanna orientalis</i>	[40]
	<i>Alkanna tinctoria</i>	[40]
Trichodesmine	<i>Heliotropium arguzioides</i>	[28]
	<i>Trichodesma africanum</i>	[40,181]
	<i>T. incanum</i>	[46]
Turkestanine	<i>Rindera baldschuanica</i>	[152]
	<i>Rindera oblongifolia</i>	[152]
	<i>Solenanthes turkestanicus</i>	[135,150]
Uplandicine	<i>Echium rauwolfii</i>	[90]
	<i>Echium setosum</i>	[96]
	<i>Echium vulgare</i>	[96]

Table 2. Cont.

Compounds	Sources	References
Uplandicine	<i>Onosma arenaria</i>	[163]
	<i>Onosma stellulatum</i>	[167]
	<i>Symphytum</i> × <i>uplandicum</i>	[180]
Uluganine	<i>Ulugbekia tshimganica</i>	[183]
Viridantine	<i>Cynoglossum furcatum</i>	[76,187]
	<i>Onosma erecta</i>	[69]
Viridiflorine	<i>Anchusa milleri</i>	[40]
	<i>Cynoglossum germanicum</i>	[77]
	<i>Cynoglossum officinale</i>	[40,84]
	<i>Cynoglossum viridiflorum</i>	[97]
	<i>Lappula spinocarpus</i>	[40]
	<i>Lindelofia olgae</i>	[150]
	<i>Lindelofia pterocarpa</i>	[151]
	<i>Lindelofia stylosa</i>	[135]
	<i>Lindelofia tshimganic</i>	[152]
	<i>Paracaryum intermedium</i>	[40]
	<i>Paracaryum regulosum</i>	[40]
	<i>Symphytum officinale</i>	[179]
	<i>Trachelanthus hissricus</i>	[29]
	<i>Trichodesma africanum</i>	[40]
	7-Viridiflorylretronecine	<i>Echium tuberculatum</i>
<i>Eritrichium rupestre</i>		[60]
<i>Nonnea lutea</i>		[60]
<i>Nonnea setosa</i>		[60]
<i>Onosma stellulatum</i>		[60]
Vulgarine	<i>Echium vulgare</i>	[11]

2. Phytochemical Analysis of PAs

Various analytical techniques have been used for extraction, separation, identification and quantification of PAs. Recently, updated reviews were published [188,189] on the analysis of PAs in plants and foods along with different methods of preparation and extraction of PAs from different matrices including plants are their parts, such as seeds, pollen, but also from honey, body fluids, and insects. In addition to column chromatography and HPLC, droplet counter current chromatography (DCCC) has been used in preparative separation of pyrrolizidine alkaloids [190]. Advantages of this method include total sample recovery, good resolution and high reproducibility. A high-speed CCC was applied for preparative separation and purification of PAs from *Amsinckia tessellata*, *Symphytum* spp. and *Trichodesma incanum* [46]. For analytical purposes high-resolution capillary GLC alone or in combination with mass spectrometry is the method of choice for free PA bases [40,59,67,70,90,91,96,163,191–195]. HPLC and HPLC-MS are also helpful but less sensitive than GLC and GLC-MS [60,93,196–199]. In addition, the resolution is much lower than for GLC but in HPLC also PA-N-Oxides can be directly analysed. The present review describes the most common analytical tools for the analysis of PAs with an emphasis of mass spectrometry (mostly based on GLC-MS analyses).

2.1. Mass Spectrometry

Mass spectrometry is an important and sensitive tool for the identification and structural determination of PAs. The advantages of mass spectrometry are high sensitivity and possibilities of combination with liquid chromatographic methods (e.g., GLC or HPLC) for the analysis of complex mixtures which usually exist in natural sources. Mass spectral data of PAs have been documented in several publications so that a comprehensive database exists. With respect to PAs, the mass spectra provide the molecular mass, type and structure of necine nucleus (saturation at 1, 2-position), sites of hydroxylation and acylation of the hydroxyl groups (as monoester and/or diester). However, MS alone does not provide all necessary structural information (especially, stereochemistry) necessary for an unambiguous assignment of the structure to an unknown compound. There is no difference between the mass spectra of the epimeric pairs e.g., the spectrum of 7-angeloylretronecine is identical to that of 7-angeloylheliotridine, the OH-groups at C-7 are β and α -oriented, respectively. The same situation exists with the stereoisomer pair echimidine and heliosupine. Echinatine, rinderine (heliotridine bases), lycopsamine, intermedine and indicine (retronecine bases) esterified at C-9 with the stereoisomeric acids, (-)-viridifloric, (+)-trachelanthic, (-)-viridifloric, (+)-trachelanthic and (-)-trachelanthic exhibit almost identical mass spectra (Figures 3–15).

Mass spectra of PAs provide important informations about the structure of necine substituents. The 1,2-unsaturated necine esterified at C-9 with a free hydroxyl group at C-7 exhibit a base peak at m/z 138, whereas acylation of C-7 (uplandicine, 7-acetyllycopsamine) provide a base peak at m/z 180. PAs with 1,2-unsaturated necines but without a hydroxyl group at C-7 (as in supinidine type) with an esterification at C-9 results in a base peak m/z 122, while the saturated necine of the same type (trachelanthamidine, isoretroncanol, lindelofidine) shows a base peak at m/z 124. 1,2-unsaturated diester PAs esterified with angelic, tiglic or senecioic at C-7 shows a base peak at m/z 220 [40,42,59,67,70,90,91,96,163,193,200,201]. The fragmentation pathway of this type of PAs starts with the cleavage of the weak allylic ester bond at C-9.

Figure 3. Mass spectrum of retronecine/heliotridin.

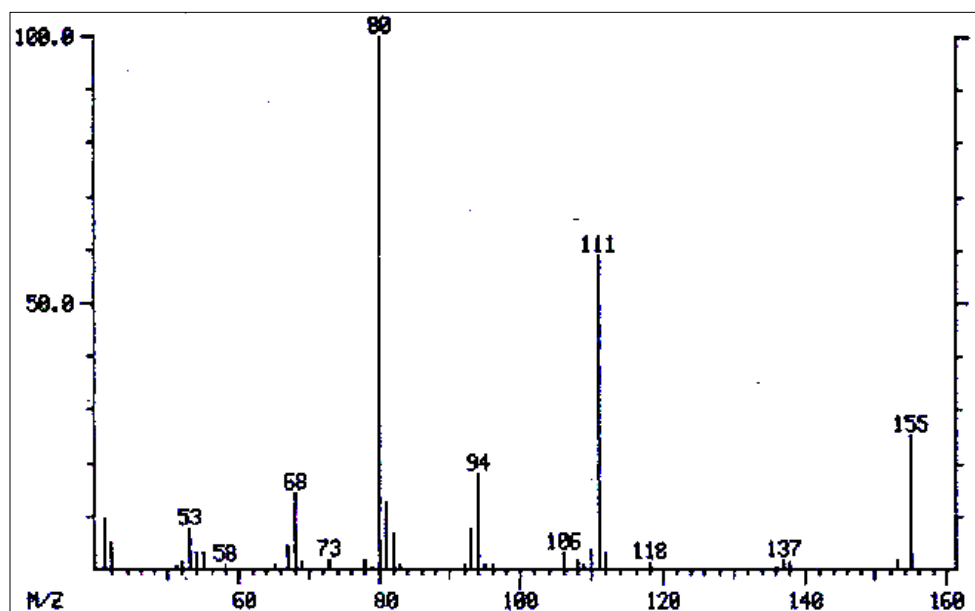


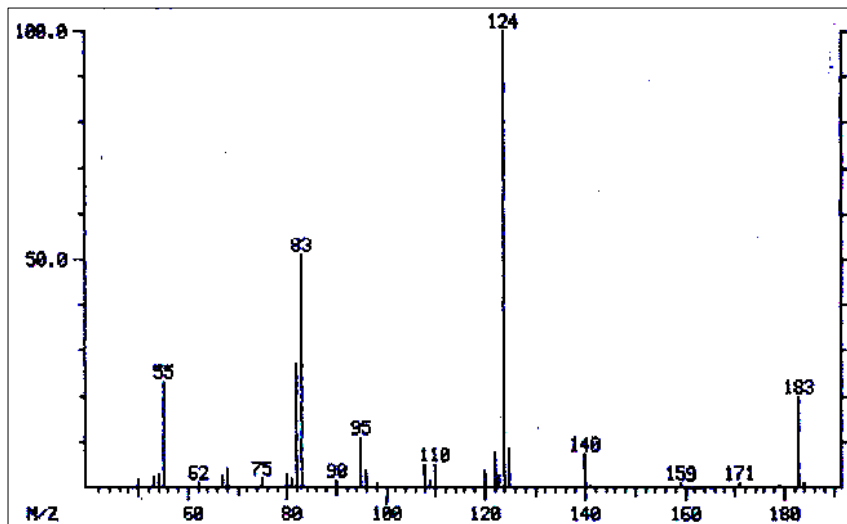
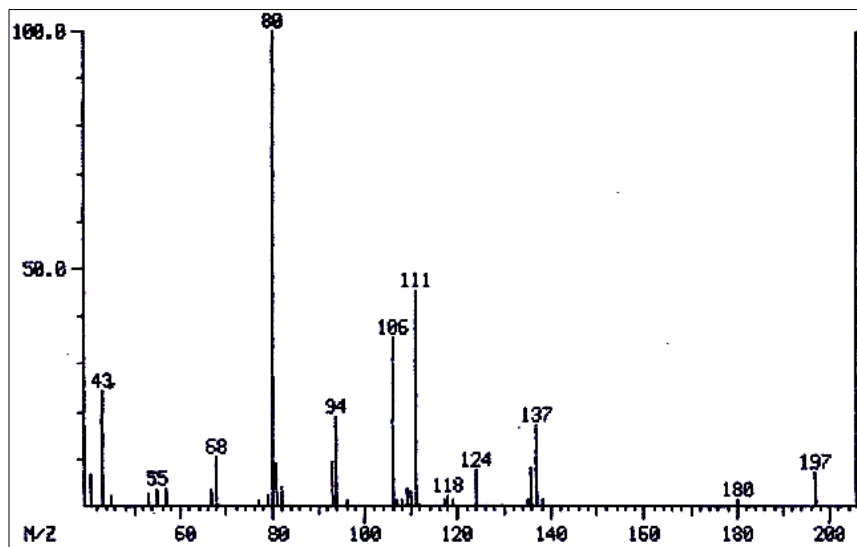
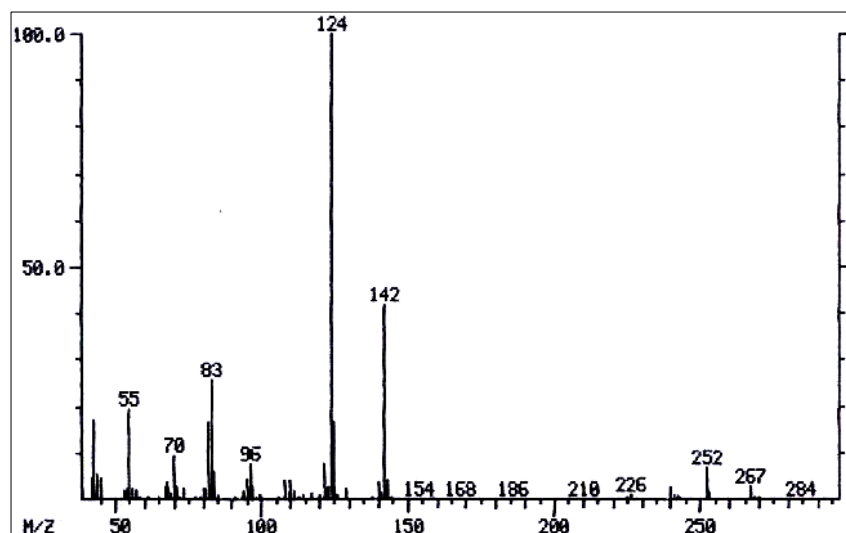
Figure 4. Mass spectrum of 9-acetyltrachelanthamide.**Figure 5.** Mass spectrum of 7-acetylretronecine/7-acetylheliotridine.**Figure 6.** Mass spectrum of viridiflorine/trachelanthamine.

Figure 7. Mass spectrum of 9-angeloyl or 9-tigloylretronecine 9-angeloyl or 9-tigloylheliotridine.

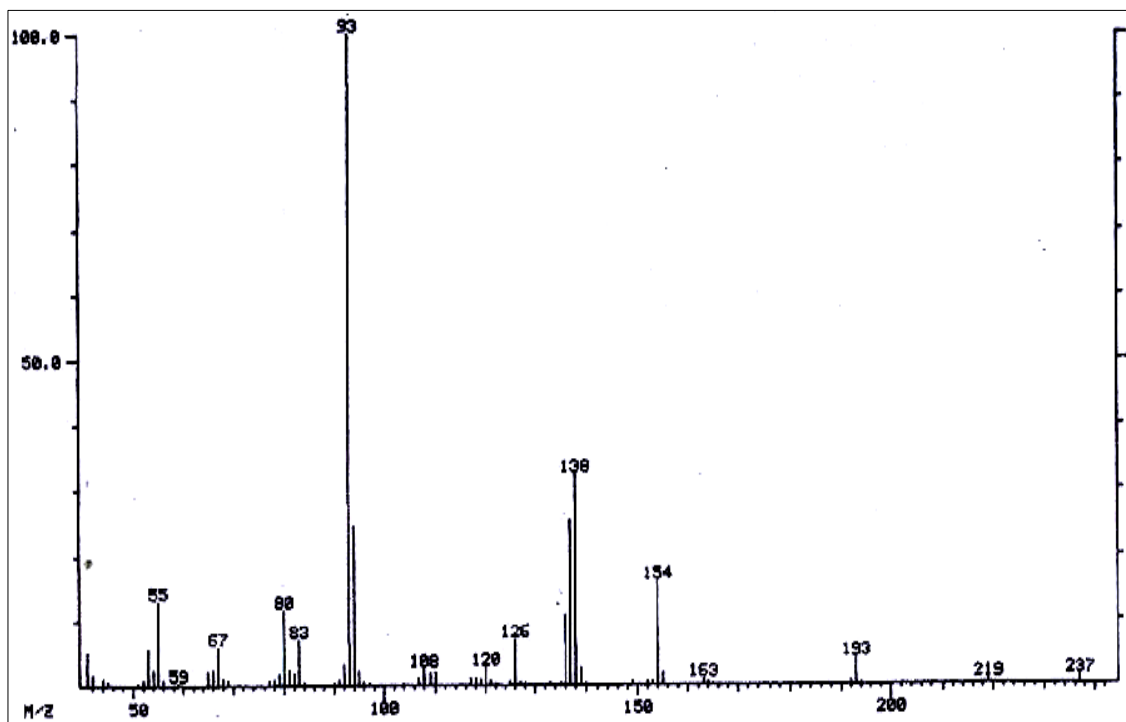


Figure 8. Mass spectrum of amabiline.

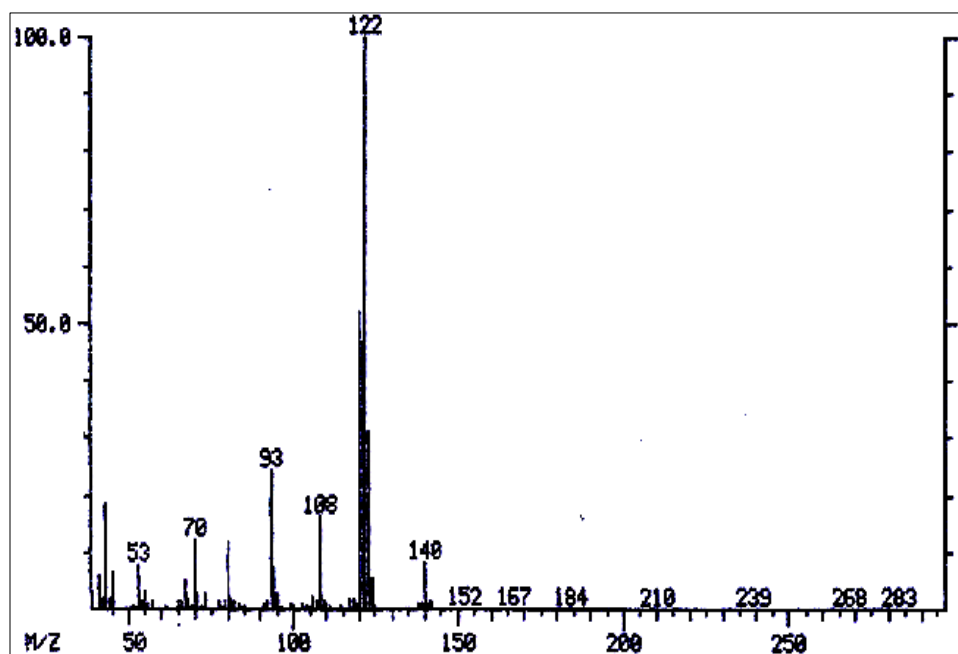


Figure 9. Mass spectrum of 9-curassavoyliheliotridine.

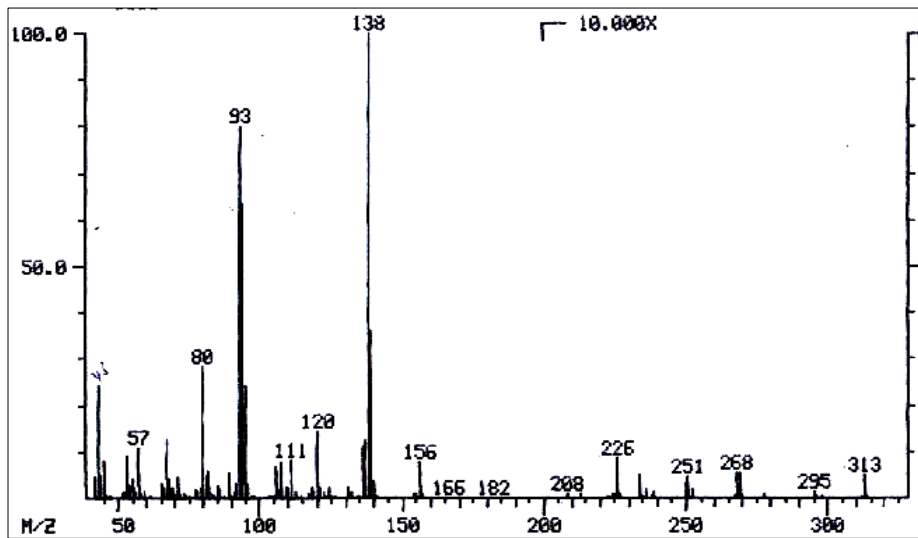


Figure 10. Mass spectrum of heliotrine.

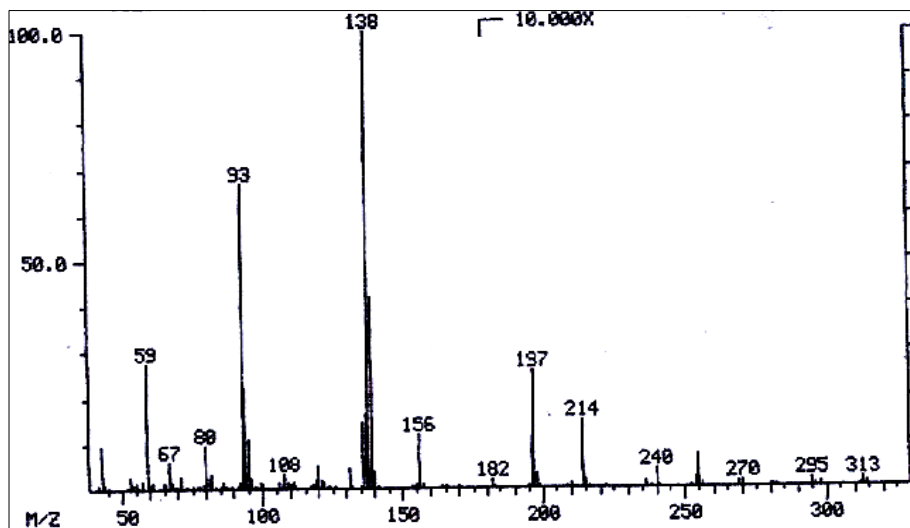


Figure 11. Mass spectrum of lycopsamine/intermediate/indicine/echinatine/rinderine.

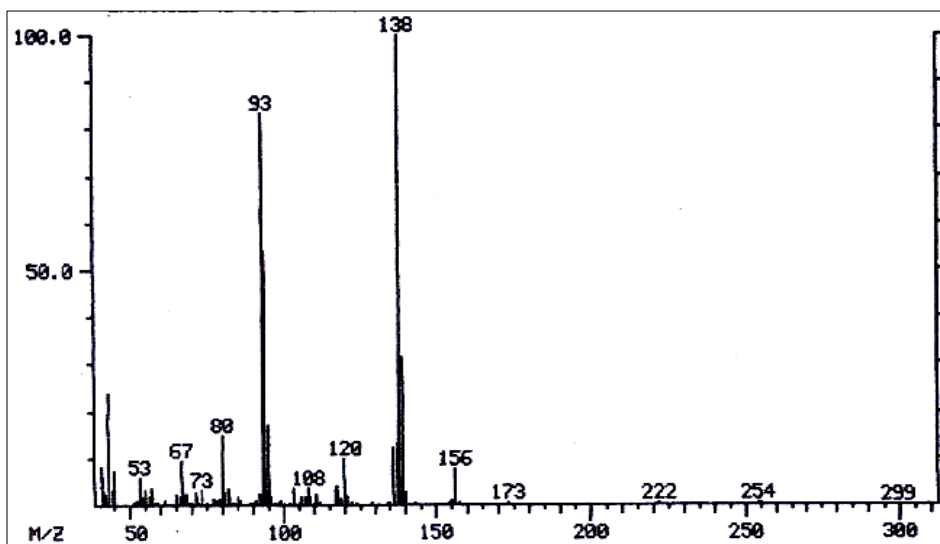


Figure 12. Mass spectrum of 7-acetylycopsamine/7-acetyl intermedine/7-acetyl indicine/7-acetyl echinatine/7-acetyl rinderine.

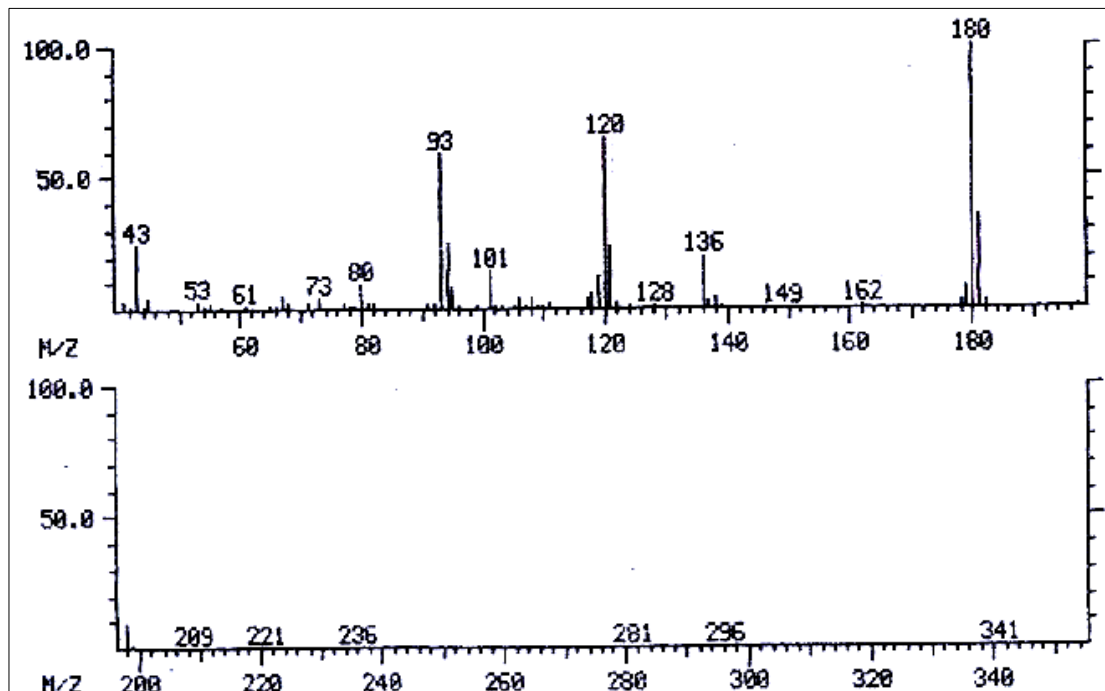


Figure 13. Mass spectrum of 3',7-diacetylycopsamine/3',7-diacetyl intermedine/3',7-diacetyl indicine/3',7-diacetyl echinatine/3',7-diacetyl rinderine.

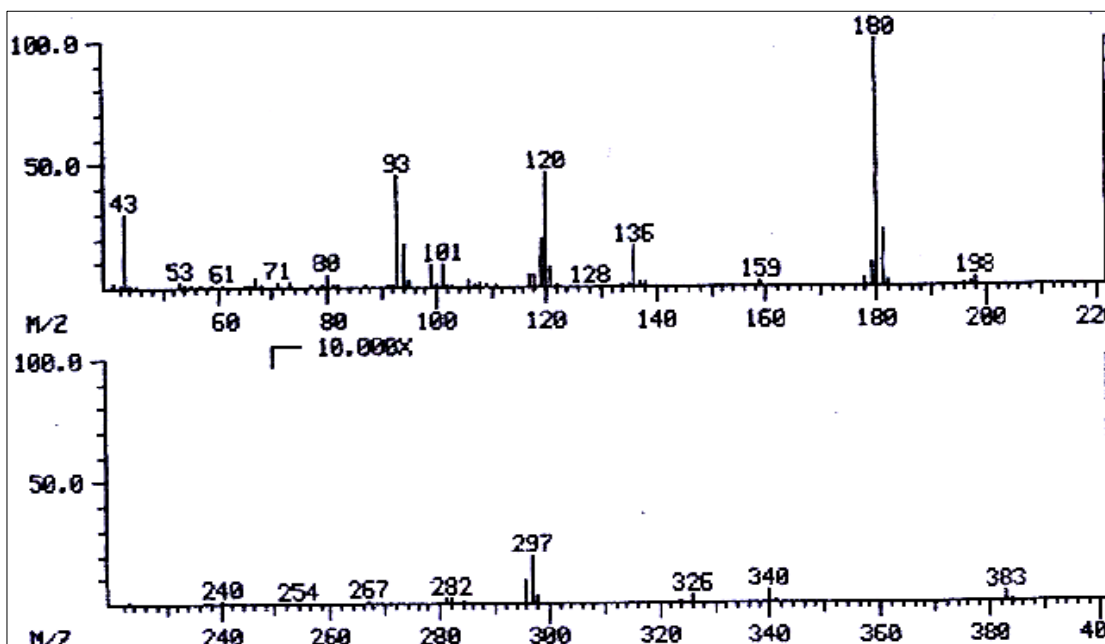


Figure 14. Mass spectrum of echimidine/heliosupine.

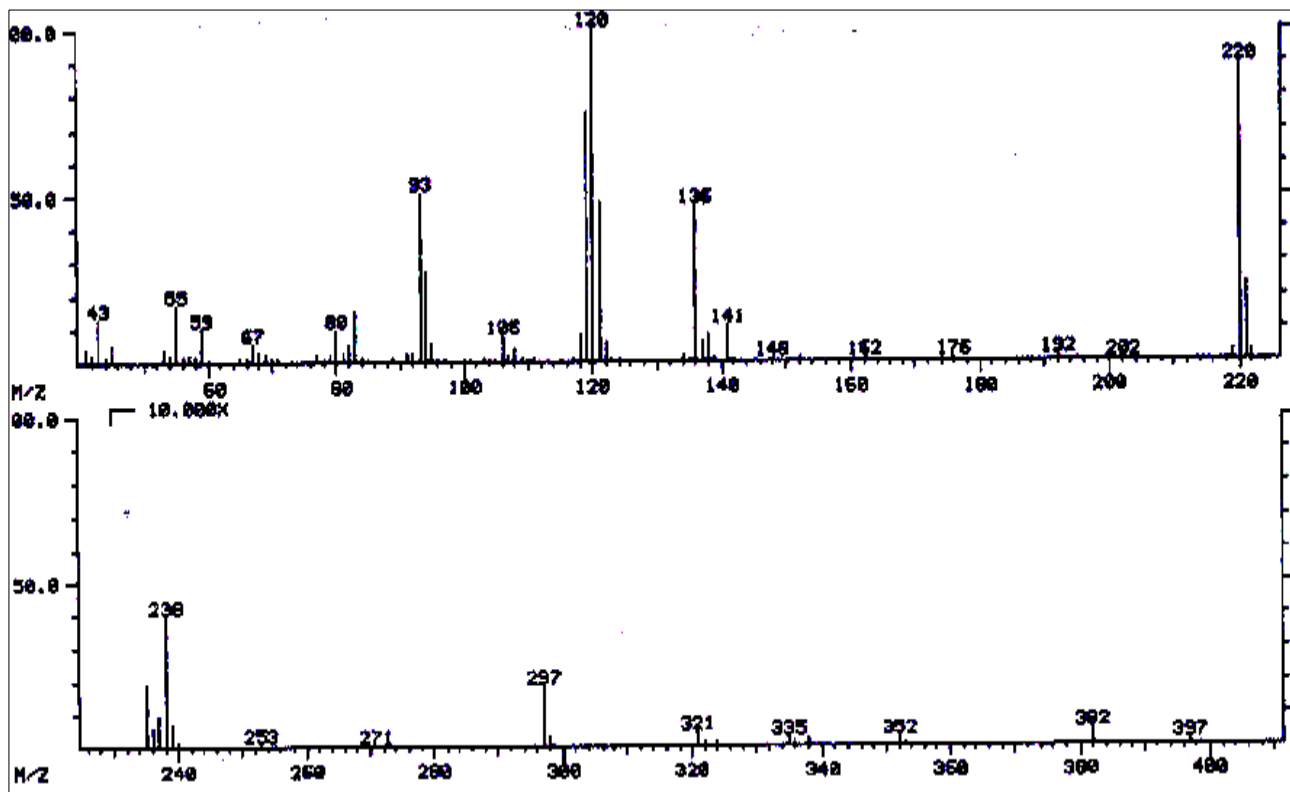
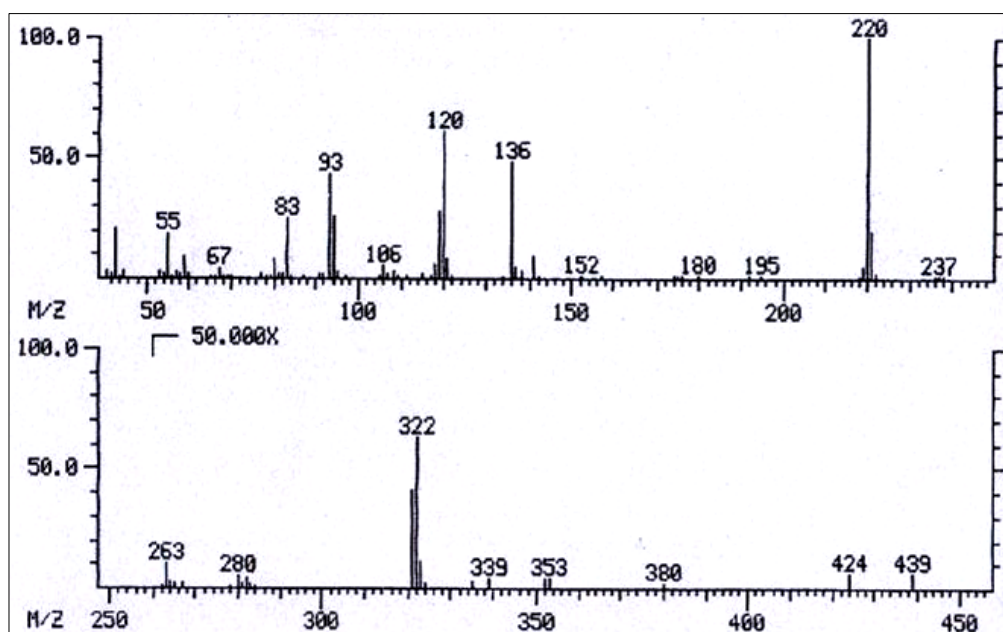


Figure 15. Mass spectrum of 3'-acetylechimidine/3'-acetylheliosupine.



In our review we have tabulated the MS data useful for the identification and structural studies of PAs in Boraginaceae; Table 3 summarizes the mass spectral data (GLC-MS, LC-MS, direct inlet) of corresponding PAs.

Table 3. Mass data of PAs (mostly derived from gas-liquid chromatography-mass spectrometry (GLC-MS) analyses) for all compounds identified in the Boraginaceae. Compounds are numbered as in Figure 16.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
1	3'-Acetylcanescine	-	441	441(0.7), 426(2.6), 355(2.4), 255(6.3), 238(62.4), 220(18.3), 180(39), 136(47), 120(100), 93(74), 80(20).	[154]
2	3'-Acetylcanescenine	-	441	441(1.2), 426(2.4), 398(1.6), 355(1.2), 255(5.7), 238(58.2), 220(20.3), 180(44.3), 136(43.4), 120(100), 93(80.3), 80(22.1).	[154]
3	7-Acetyl-9-curassavoylheliotridine	2275	355	295(0.1), 268(0.2), 198(8), 181(36), 180(100), 136(22), 121(26), 120(84), 119(12), 95(15), 93(35), 80(17), 67(10), 57(12), 45(9), 43(48).	[40]
4	7-Acetyl-9-(2,3-dihydroxybutryl) retronecine	2092	299	239(3), 181(20), 180(100), 136(20), 120(59), 101(20), 94(32), 93(73), 80(12), 67(5), 55(5), 43(15).	[163]
5	7-Acetyl-9-(2,3-dimethylbutryl) retronecine	1947**	295	235(8), 180(100), 136(20), 120(36), 101(30), 94(30), 93(65), 80(8), 43(42).	[163]
6	3'-Acetylechinate	2220	341	326(0.1), 298(1), 255(2), 254(2), 181(2), 156(4), 139(21), 138(100), 137(10), 136(10), 120(6), 99(6), 94(20), 93(71), 80(8), 67(5), 43(22).	[84]
7	7-Acetylechinate	2235	341	341(0.1), 281(2), 198(6), 181(39), 180(100), 136(18), 121(35), 120(70), 119(28), 101(9), 94(18), 93(55), 80(7), 43(33).	[67]
8	3'-Acetylechiimine	2245*	423	423(2), 380(3), 338(3), 337(6), 336(3), 323(2), 280(3), 263(3), 256(2), 238(5), 237(6), 221(34), 220(100), 219(15), 159(5), 141(19), 138(12), 136(54), 121(20), 120(76), 119(34), 106(12), 94(42), 93(56), 83(27), 80(15), 59(3), 55(34), 53(17).	[42]
9	3'-Acetylechimidine	2640	439	439(0.1), 424(0.1), 322(1), 238(2), 221(25), 220(100), 219(3), 138(5), 137(6), 136(49), 121(8), 120(61), 119(28), 106(6), 94(24), 93(46), 83(14), 59(11), 55(13).	[91]
10	5'-Acetyleuropine	-	371	156(18), 138(100), 94(36), 93(75), 59(74).	[138]
11	7-Acetyleuropine	-	371	371(2.7), 356(1), 311(3), 282(5), 180(100), 120(72), 93(65), 80(17), 59(95).	[110]
12	3'-Acetylfurcatine	3188*	425	223(28), 222(100), 143(10), 136(36), 121(15), 120(82), 94(27), 93(61), 85(21), 80(7), 57(63).	[42]
13	3'-Acetylheliosupine	2640	439	424(0.1), 321(1), 221(28), 220(100), 141(10), 138(4), 137(5), 136(45), 121(14), 120(89), 119(82), 106(7), 94(21), 93(40), 83(11), 80(5), 59(8), 55(11), 43(22).	[67]
14	7-Acetyl-9-(2-hydroxy-3-methylbutryl) retronecine	2024**	297	237(5), 180(100), 136(25), 120(52), 119(20), 101(25), 94(45), 93(95), 80(15), 43(35).	[163]
15	3'-Acetyllindicine	2195	341	341(2), 255(2), 181(5), 138(100), 93(48), 43(10).	[158]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
16	3'-Acetylintermedine	2255	341	341(5), 298 (4), 255 (16), 139 (20), 138(100), 137 (12), 136 (12), 94 (30), 93 (71), 80 (10), 43 (21).	[40]
17	7-Acetylintermedine	2220	341	296(4), 281(3), 181(40), 180(100), 136(25), 121(30), 120(78), 119(15), 101(19), 95(10), 94(30), 93(73), 80(11), 43(40).	[40]
18	5'-Acetyllassiocarpine	-	453	363, 335, 321, 263, 220(100), 141, 136, 121, 120, 119, 106, 94, 93, 83, 80.	[186]
19	3'-Acetylithosenine	-	457	457(0.78), 442(2), 339(1), 255(2), 238(100), 237(5), 222(10), 220(25), 138(30), 137(8), 136(49), 121(36), 120(75), 119(36), 95(9), 94(34), 93(57), 80(12).	[156]
20	3'-Acetyllycopsamine	2255	341	341(5), 298(4), 255(16), 139(20), 138(100), 137(12), 136(12), 94 (30), 93(71), 80 (10), 43(21).	[40]
21	7-Acetyllycopsamine	2230	341	341(1), 296(4), 281(3), 181(32), 180(100), 136(20), 121(35), 120(70), 119(11), 101 (19), 95(10), 94 (28), 93(61), 80(10), 43(36).	[91]
22	7-Acetyl-9-(2-methylbutyryl) retronecine	1914**	281	221(12), 195(5), 180(100), 136(25), 120(42), 119(15), 101(35), 94(45), 93(80), 80(13), 67(100), 57(18), 53(5), 43(23).	[163]
23	3'-Acetylmyscorpine	3290*	423	221(30), 220(100), 136(47), 120(67), 119(35), 94(39), 93(51), 83(32), 80(19), 55(39).	[42]
24	7-Acetylretronecine	1532**	197	180(3), 137(12), 111(40), 106(30), 94(20), 80(100), 68(3), 43(30).	[163]
25	3'-Acetylrrinderine	2222	341	326(0.1), 298(1), 255(1), 254(0.5), 181(5), 156(5), 139(30), 138(100), 137(17), 136(17), 120(10), 99(10), 95(9), 94(35), 93(95), 80(13), 67(9), 43(36).	[70]
26	7-Acetyl-9-(sarracinoyl) retronecine	2125	295	235(1), 197(32), 196(10), 181(8), 180(55), 179(15), 136(34), 121(12), 120(42), 119 (20), 101(19), 94(40), 93(100), 80(15), 67(6), 53(9), 43(20).	[40]
27	7-Acetylscorpioidine	-	423	423(0.8), 181(23), 180(92), 179(17), 136(23), 121(10), 120(57), 119(45), 95(6), 94(35), 93(57), 83(100), 80(15), 55(39), 43(30).	[159]
28	3'-Acetylsupinine	2080**	325	284(.02), 299(10), 136(10), 122(100), 120(48), 108(13), 101(13), 93(50), 80(13), 70(9), 53(6), 43(15).	[163]
29	3'-Acetyltessellatine	3064*	341	341(41), 324(10), 323(10), 299(2), 280(8), 255(2), 254(4), 248(2), 238(2), 237(5), 236(17), 198(8), 181(4), 180(2), 156(7), 154(12), 138(22), 137(28), 136(27), 124(23), 120(63), 111(66), 108(30), 106(61), 99(17), 94(35), 93(14), 80(100), 55(10), 53(10).	[42]
30	9-Acetyltessellatine	2962*	341	341(7), 299(6), 282(11), 281(15), 248(3), 238(15), 237(16), 236(14), 198(18), 181(12), 180(10), 179(9), 153(13), 138(49), 136(45), 121(26), 120(100), 119(32), 108(11), 106(12), 94(52), 93(89), 80(28), 53(11).	[42]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
31	3'-Acetyltrachelanthamine	-	327	327(1), 284(2), 240(6), 184(6), 142(27), 125(38), 124(100), 84(14), 83(59), 82(54).	[128]
32	9-Acetyltrachelanthamidine	1395	183	140(8), 125(8), 124(100), 110(5), 95 (10), 83(50), 82 (27), 55(23).	[40]
33	3'-Acetylviridiflorine	2767*	327	327(3), 284(6), 268(2), 267(2), 241(5), 240(9), 225(4), 184(4), 159(2), 142(21), 140(4), 125(17), 124(100), 83(14), 82(12), 55(19).	[42]
34	9-(3'-Acetylviridifloryl)retronecine	-	341	341(4.7), 255(3), 182(5), 157(4), 138(100), 120(10), 93(92), 85(4), 83(20), 80(16), 43(38).	[119]
35	9-(3'-Acetyl)viridiflorylturneformidine (or isomer)	3050*	343	343(5), 325(4), 300(12), 299(5), 257(14), 256(50), 212(13), 200(15), 197(14), 159(10), 158(36), 141(19), 140(30), 138(16), 122(21), 120(33), 117(10), 106(12), 96(44), 95(90), 83(11), 82(100), 69(17), 55(32).	[42]
36	7-Acetylvulgarine	-	439	440(M ⁺ + 1), 422(40), 380(15), 358(5), 340(65), 296(42), 282(85), 180(100).	[11]
37	Amabiline	1985, 2652*	283	383(1), 140(8), 123 (30), 122(100), 121(46), 120(51), 108(17), 93(25), 80(13), 70 (17), 53(7), 45(6), 43(19).	[67]
38	Anadoline	-	381	381(6), 204(6), 167(6), 149(23), 139(22), 138(93), 137(45), 136(33), 120(17), 119(17), 118(13), 117(18), 111(12), 109(15), 100(15), 97(17), 95(27), 94(55), 93(88), 85(25), 83(100), 82(17), 81(27), 80(27), 73(14), 71(37), 70(17), 67(27), 57(73), 56(17), 55(83), 54(13), 53(20).	[202]
39	7 α -Angeloyl-1-chloromethyl-2-dihydropyrrolizidine	1815	255	220(40), 172(15), 155(45), 136(23), 130(24), 129(32), 128(63), 121(11), 120(94), 119 (24), 106(30), 94 (100), 93(20), 83(20), 80(17), 67(8), 55(35).	[70]
40	7-Angeloyl-9-(2,3-dihydroxybutyryl)heliotridine	2333	339	339(1), 324(1), 294(1), 239(6), 222(25), 221(25), 220(65), 219(8), 138 (20), 137(10), 136(81), 121(24), 120(100), 119(85), 106(15), 94(50), 93(85), 83(24), 80(18), 75(2), 57(10), 55(25), 45(10).	[67]
41	7-Angeloyl-9-(2,3-dihydroxybutyryl)retronecine	2315	339	339(1), 239(5), 238(5), 237(5), 221(25), 220(99), 219(15), 141(20), 138(10), 137(11), 136 (100), 121(15), 120(83), 119(34), 106(10), 94(55), 93(95), 83(41), 80(20), 75(2), 57(10), 55(40), 45(10).	[96]
42	7-Angeloyl-9-(2,3-dihydroxypropanoyl)retronecine	2300	325	294(0.5), 237(5), 255(9), 221(10), 220(67), 219(16), 141(22), 138(5), 137(11), 136(100), 121(11), 120(57), 119(40), 106(10), 94(62), 93(95), 83(37), 80(17), 55(32).	[40]
43	7-Angeloyl-1-formyl-6,7-dihydro-5H-pyrrolizidine	1920	233	215(3), 150(100), 134(92), 133(35), 122(4), 106(15), 105(38), 104(15), 83(10), 79(16), 55(20).	[67]
44	7-Angeloyl-9-(hydroxypropanoyl)retronecine	2053	307	221(13), 220(95), 207(24), 181(8), 141(30), 137(10), 136(100), 120(53), 119 (24), 106(10), 94(63), 93(77), 83(43), 80(21), 67(9), 55(41), 43 (26).	[40]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
45	7-Angeloylechinate	2467	381	336(2), 281(1), 238(11), 221(42), 220(86), 141(11), 138(11), 137(9), 136(55), 121(78), 120(100), 119(60), 117(4), 106(9), 99(3), 94 (30), 93(52), 83(17), 80(10), 55(17), 45(8), 43(21).	[67]
46	7-Angeloylheliotridine	1820	237	219(1), 154(2), 137(42), 136(20), 124(25), 111(35), 106(86), 94(25), 83(10), 80(100), 68(10), 55(20).	[70]
47	7-Angeloylheliotine	-	395	395(5), 295(7), 220(100), 136(57), 120(80), 119(70), 93(43), 83(34), 59(55), 43(18).	[127]
48	7-Angeloyllycopsamine	2460*	381	381(0.1), 336(0.9), 281(0.5), 238(0.5), 220(100), 136(65), 121(40), 120(90), 94(40), 93(85), 83(50), 80(15), 55(48).	[90]
49	7-Angeloyl-9-(2-methylbutyryl)heliotridine	2180	321	321(0.5), 221(43), 220 (70), 195(5), 141(26), 138(4), 137(9), 136(85), 121(13), 120(100), 119(65), 106(13), 94(59), 93(71), 83 (23), 80(15), 67(4), 57(27), 55(30).	[67]
50	7-Angeloyl-9-(2-methylbutyryl)retronecine	2155	321	221(35), 220(100), 195(5), 141 (25), 138(3), 137(9), 136(90), 121(6), 120(53), 119(20), 106(8), 94(50), 93(70), 83(35), 80(15), 57(20), 55(35).	[96]
51	7-Angeloylretronecine	1787	237	237(2), 219 (3), 204(0.5), 191(1), 154(2), 138(5), 137(23), 136(18), 124(23), 111(38), 106(40), 94(20), 93(6), 83(11), 80(100), 55(22).	[96]
52	9-Angeloylretronecine	1797	237	237(1), 219(0.5), 193(3), 154(16), 138(32), 137(25), 136(10), 126(7), 120(2), 108(2), 94(25), 93(100), 83(8), 80(10), 55(13).	[96]
53	7-Angeloylrinderine	2465	381	381(0.1), 336(2), 281(1), 238(10), 221(34), 220(80), 141(11), 138(10), 137(9), 136(53), 121(70), 120(100), 119(59), 117(4), 106(10), 94(28), 93(50), 83(15), 80(10), 55(17), 45(8), 43(25).	[67]
54	9-Angeloyltrachelamthamidine	1700	223	140(1), 125 (30), 124(100), 123(20), 122(15), 110(4), 95(13), 83(45), 82(16), 70(6), 55(27).	[40]
55	9-Angeloyl-7- viridiflorylretronecine	-	381	220(8.3), 138(7.3), 137(9.8), 136(9.9), 120(28.6), 117(50), 106(29), 94(34), 93(23.1), 91(34.6), 79(40.8), 67(39.6), 64(81.8), 60(31), 58(57), 57(85), 55(100).	[60]
56	Asperumine	-	397	380, 336, 220, 138, 120.	[203]
57	9-(Butyryl-2-ene) supinidine	1674**	207	180(5), 159(7), 157(7), 122(100), 121(6), 120(23), 108(6), 93(15), 80(17), 71(25), 57(7), 53(11), 45(11), 43(14).	[163]
58	Canescine	-	399	399(0.4), 384(4), 355(1), 338(0.3), 256(10), 238(66), 220(21), 180(11.6), 136(42), 120(100), 93(65), 80(20).	[154]
59	Canescenine	-	399	399(0.1), 384(1.6), 355(0.4), 338(0.3), 256(9.6), 238(67.5), 220(20.6), 180(14.7), 136(45.1), 120(100), 93(61.6), 80(20.2).	[154]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
60	Coromandaline	-	285	285(2), 267(7), 241(3), 240(9), 142(65), 125(23), 124(100), 83(28), 82(18).	[140]
61	Coromandalinine	-	283	283(0.8), 239(0.4), 238(0.3), 140(7), 123(27), 122(100), 121(35), 120(40), 108(13), 94(8), 93(20.5),	[140]
62	Cryptanthine	-	353	354[M ⁺ +1](1), 272(2), 254(3), 238(2), 138(2), 120(100), 118(2).	[65]
63	Curassanecine	-	157	126(14), 98(10), 83(100) 82(23).	[117]
64	Curassavine	-	299	299(0.7), 281(1.4), 255(2.6), 254(5), 142(80), 125(27), 124(100).	[140]
65	Curassavinine	-	297	297(0.3), 253(0.1), 252(0.1), 241(0.1), 239(0.1), 140(8), 123(31), 122(100), 121(44), 120(41), 108(13), 94(6.4), 93(20).	[140]
66	9-Curassavoylheliotridine	2190	313	295(2), 269(0.5), 268(0.5), 251(0.5), 226(0.9), 156(8), 139(35), 138(100), 120(15), 111(9), 106(8), 95(25), 94(64), 93(80), 80(28), 67(13), 57(11), 45(8), 43(25).	[40]
67	Cynaustine	-	283	C ₁₅ H ₂₅ NO ₄ , 122(100).	[68]
68	Cynaustraline (or stereoisomer)	2682*	285	285(2), 267(4), 252(5), 242(1), 241(1), 240(3), 226(1), 142(34), 125(15), 124(100), 83(24), 82(14), 55(25).	[42]
69	Cynoglossamine	-	445	147(100), 138(27), 119(17), 93(23).	[138]
70	5-Deoxylasiocarpine	-	395	396[M + H] ⁺ (2), 295(5.5), 363(1), 220(80), 120(83), 93(68), 83(32).	[123]
71/72	3',7-Diacetylintermedine/ 3',7-Diacetyllycopsamine	2340	383	340(5), 297(10), 296(10), 181(22), 180(100), 136(18), 121(8), 120(47), 119(20), 101(10), 99(10), 94(18), 93(47), 80(5), 43(30).	[40]
73	3',9-Diacetyltessellatine	3090*	383	383(2), 342, 341(37)(7), 324(21), 323(10), 297(8), 296(6), 280(10), 238(2), 237(6), 236(18), 198(10), 181(7), 180(4), 179(8), 154(14), 153(22), 138(20), 136(49), 121(18), 120(100), 119(55), 108(12), 106(19), 99(13), 94(37), 93(82), 80(25), 53(11).	[42]
74	5,6-Dihydro-7,9-dimethoxy-7H-pyrrolizine	1415**	181	150(90), 134(5), 120(100), 119(35), 106(12), 91(3), 79(5).	[163]
75	Dihydroechinatine	-	301	MS ² , 284, 258, 240, 140, 122, 96.	[167]
76	thero-2",3"- Dihydroxyechiumine	-	415	415(0.5), 371(2), 254(56), 210(26), 166(5), 138(30), 136(37), 120(100), 93(70).	[63]
77	Dihydroxytriangularine	2525	369	338(1), 324 (2), 269(30), 252(30), 237(40), 221(25), 220(100), 219(10), 141(20), 138(8), 137(10), 136(80), 121(20), 120(80), 119(30), 106 (8), 95 (9), 94 (45), 93(81), 83(39), 80(10), 55(28).	[40]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
78	Dihydroxytriangularicine	2525	369	338(0.1), 324 (0.1), 269(4), 252 (4), 237(5), 221(24), 220(100), 219(3), 141(28), 138(6), 137(8), 136(67), 121(24), 120(75), 119(35), 106(8), 95(8), 94(47), 93(90), 83(41), 80(11), 55(24).	[40]
79	Echihumiline	2578	397	397(0.1), 382 (0.2), 352 (0.1), 338 (0.1), 321 (0.1), 297 (2), 238 (2), 221 (20), 220 (100), 219 (4), 138 (6), 137 (6), 136 (40), 121 (15), 120 (39), 119 (16), 106 (4), 94 (20), 93 (30), 83 (36), 80 (6), 59 (5), 55 (6).	[91]
80	Echimidine	2560	397	397(0.1), 382 (0.1), 352 (0.1), 297(2), 221(21), 220(100), 219(5), 138(5), 137(6), 136(48), 121(26), 120(75), 119(30), 106(5), 94(30), 93 (61), 83(39), 80(10), 59(10), 55(25), 43(18).	[96]
81	Echimidine isomer (tigloyl)	2580	397	397(0.1), 382 (0.1), 297(2), 238 (3), 221(21), 220(100), 219(3), 138(5), 137(6), 136(48), 121(28), 120(62), 119(23), 106(5), 94(28), 93 (46), 83(30), 80(10), 59(10), 55(20), 43(18).	[96]
82	Echinatine	2175	299	284(0.1), 254(1), 156(10), 139(30), 138 (100), 137(7), 136(4), 95(9), 94(25), 93 (46), 80(7), 67(5), 53(3), 43(12).	[70]
83	Echiumine	3178*	381	381(0.4), 338(1), 337(1), 336(1), 281(2), 255(1), 238(9), 237(2), 221(35), 220(100), 141(16), 138(8), 136(47), 121(32), 120(69), 119(20), 106(7), 94(39), 93(50), 83(28), 80(17), 59(1), 55(37), 53(9).	[42]
84	Echiuplatine		381	383[M ⁺ +1](3), 382(68), 365(1), 364(1), 322(2), 320(24), 300(5), 282(7), 280(1), 238(4), 220(51), 138(2), 120(100), 118(2).	[65]
85	Echiupinine	-	381	381(0.3), 337(1), 336(1), 282(0.2), 281(2), 212(38), 220(100), 136(43), 121(33), 120(55), 119(19), 118(18), 117(14), 103(16), 94(24), 93(47),	[95]
86	Echivulgarine	-	479	480(M ⁺ + 1), 462(35), 418(10), 398(10), 380(90), 336(40), 322(100), 220(70).	[11]
87	Ehretinine	-	275	275, 140(100), 123, 97.	[100]
88	2",3"-Epoxyechiumine	-	397	254(9), 237(33), 236(100), 164(17), 157(4), 138(4), 136(19), 121(24), 120(25), 94(27), 93(44), 80(12), 71(4), 43(30).	[63]
89	<i>Erythro</i> -2",3"-chloro-2"-hydroxyechiumine	-	435	435(0.5), 274(37), 273(32), 272(92), 254(10), 236(13), 208(9), 138(10), 136(25), 121(26), 120(100), 94(32), 93(45), 80(19), 71(19).	[63]
90	1 α -2 α -Epoxy-1 β -hydroxymethyl-8 α -pyrrolizidine	-	155	126(4), 124(13), 96(10), 80(4), 71(50), 70(100), 68(10), 67(5), 56(6), 55(65).	[106]
91	Europine	2217	329	314(1), 256(5), 240(25), 239(20), 156(10), 139(20), 138(100), 120(5), 94(20), 93(50), 80(10), 67(4), 59(20), 43(5).	[52]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
92	Floridanine	-	441	426, 397, 382, 168, 152, 151(100), 150, 149, 123, 122, 110, 96, 94.	[62,204]
93	Floridimine	-	301	301(1), 239(8), 226(7), 142(36), 124(100), 95(12), 94(10), 83(55), 55(23).	[128]
94	Floridine	-	343	343(1), 328(2), 284(1), 240(2), 239(3), 225(10), 142(8), 124(100), 83(27).	[128]
95	Floridinine	-	301	301(1), 242(5), 239(7), 226(5), 167(1), 142(46), 125(19), 124(100), 122(8), 110(6), 96(8), 95(7), 83(36), 82(24), 70(12), 59(12).	[128]
96	Furcatine	3138*	383	383(0.2), 339(1), 281(1), 240(6), 223(35), 222(100), 143(18), 136(33), 121(27), 120(75), 119(21), 94(44), 93(65), 85(13), 80(19), 74(8), 73(5), 60(1), 57(46).	[42]
97	Heleurine	1970	297	239(1), 198(3), 181(6), 140(15), 131(6), 123(30), 122(100), 120(60), 119(70), 108(16), 93(17), 80(10), 70(11), 59(26).	[109]
98	Helibracteatine	-	255	255(0.5), 238(6), 237(1), 224(9), 156(43.4), 155(45.5), 138(16.3), 122(2.3), 111(99.7), 99(31), 98(100), 82(35).	[112]
99	Helibractinecine	-	173	173(22), 156(4), 155(11), 142(7), 129(10), 124(1), 112(5), 99(83), 98(83), 95(6), 83(7), 82(100).	[111]
100	Helibracteatinecine	-	173	173(20), 156(4.5), 155(14), 142(3), 129(12), 124(1), 112(5), 99(85), 98(100), 82(83.5).	[112]
101	Helibracteatinine	-	255	255(2), 238(3), 237(3.5), 224(9), 198(7), 181(60), 156(16), 155(93), 154(10), 124(12), 122(21), 100(23), 98(20), 83(23), 82(100).	[112]
102	Helifoline	-	255	237(3), 156(5), 138(11), 137(3), 112(27), 111(100), 99(9), 98(42), 94(41), 83(9), 82(20), 80(24).	[136]
103	Helifolinecine	-	173	155(9.5), 129(67), 124(3), 116(6), 112(8), 98(100), 82(59), 80(10).	[136]
104	Helindicine	-	281	281(35), 207(100), 191(15), 149(37), 135(33), 109(34), 97(73), 95(55), 83(57), 81(46).	[130]
105	Heliocoromandaline	-	285	285(1), 267(4), 252(4), 240(6), 142(41), 125(17), 124(100), 84(63), 83(20), 82(15).	[117]
106	Heliocurassavine	-	299	299(1), 284(1), 281(1), 255(3), 254(10), 252(8), 243(7), 226(8), 142(48), 124(100), 83(56), 82(40).	[117]
107	Heliocurassavicine	-	285	285(1), 267(3), 252(3), 240(3), 142(49), 125(22), 124(100), 84(63), 83(58), 82(41).	[117]
108	Heliocurassavinine	-	285	285(1), 267(4), 252(4), 240(3), 142(55), 125(24), 124(100), 84(22), 83(48), 82(48), 81(36).	[117]
109	Heliospathine	-	313	313(1.3), 269(2), 268(1), 156(12), 139(43), 138(100), 137(15), 120(11), 95(20), 94(57), 93(75), 80(10).	[140]
110	Heliospathuline	-	299	299(14.7), 282(6), 281(16.5), 238(18), 237(19), 236(20), 156(38), 139(30), 137(36), 136(20), 124(19), 120(60), 111(100), 108(51), 106(63), 94(41), 93(13), 80(78), 45(12).	[140]
111	Heliosupine	2553	397	382(0.1), 352(0.1), 297(2), 238(4), 221(29), 220(100), 141(11), 138(10), 137(8), 136(50), 121(40), 120(95), 119(70), 106(10), 94(26), 93(52), 83(12), 80(10), 59(10), 55(15), 43(15).	[70]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
112	Heliotridine	1447	155	138(2), 111(55), 94(18), 80(100), 68(15).	[40]
113	Heliotridine 2S-hydroxy-2S(1S-hydroxyethyl-4-methyl-pentanoyl ester	-	313	MS2: 269, 270, 224, 156, 138, 120, 94.	[50]
114	Heliotrine	2100	313	255(0.3), 214(0.5), 197(1), 156(5), 139(22), 138(100), 136(13), 120(7), 94(41), 93(83), 80(40), 59(85).	[52]
115	Heliovicine	-	285	267(5), 252(5), 240(4), 226(3), 175(1), 142(35), 124(100), 96(11), 95(9), 83(25), 82(20), 55(33).	[128]
116	Heliscabine	-	255	255(4), 156(42), 138(12), 111(100), 99(33), 98(92), 82(77), 80(10).	[139]
117	Hydroxymyoscorpine	-	397	397(0.2), 382(0.5), 338(0.1), 297(3.6), 221(21.3), 220(100), 136(40), 121(16), 120(41), 119(16.6), 94(18.4), 93(36).	[95]
118	7-(Hydroxy-methylbutyryl)-9- viridifloryl retronecine	2560**	399	384(2), 354(0.4), 296(0.3), 282(2), 256(6), 239(21), 238(55), 138(15), 136(21), 121(35), 120(100), 108(2), 101(5), 95(10), 94(20), 93(42), 83(5), 80(6), 73(5), 67(3), 59(12), 55(0.5), 43(25).	[59]
119	Ilamine	-	313	314(M ⁺ +1, 18), 224(6), 139(3), 122(52), 120(25), 93(20), 80(8), 59(100).	[115]
120	Incanine	-	337	294(2), 250(4), 222(10), 206(8), 155(5), 136(100), 120(77), 119(85), 94(42), 93(56), 80(26), 53(17), 43(69).	[46]
121	Indicine	2126	299	255(4), 156(11), 138(100), 93(95).	[158]
122	<i>Isoechinatine</i> (9-(+)- viridiflorylheliotridine)	-	299	299(11), 156(10), 139(33), 138(100), 137(14), 94(32), 93(68), 80(18).	[75,138]
123	<i>Iso lycopsamine</i>	-	299	281(12.3), 236(10.3), 138(67), 137(42), 136(34), 124(21), 121(15), 120(70), 119(15), 118(15), 117(14), 111(68), 110(21), 109(11), 108(49), 106(81), 95(17), 94(43), 93(28), 80(100).	[133]
124	<i>Isoretronocanol</i> enantiomer	1883*	141	141(20), 140(9), 124(13), 110(12), 108(11), 83(100), 82(56), 70(10), 68(11), 55(48).	[42]
125	9-(3'-Isovaleryl)viridifloryl retronecine	-	383	383(0.2), 255(3), 240(3), 223(5), 20194), 138(100), 120(10), 93(66), 85(28), 80(10), 57(19), 43(10),	[119]
126	Intermedine	2133	299	156(9), 139(35), 138(100), 137(13), 136(13), 120(10), 95(15), 94(50), 93(80), 80(14), 67(9), 45(7), 43(18).	[40]
127	Lactodine	-	227	227(9), 138(32), 137(41), 124(15), 111(60), 106(21), 94(44), 80(100).	[76,187]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
128	Lasiocarpine	-	411	396(2), 311(4), 279(5), 221(43), 220(11), 137(20), 136(49), 124(22), 120(74), 119(42), 106(15), 95(49), 93(23), 93(33), 83(39).	[71]
129	Latifoline	-	393	393(6), 293(9), 221(10), 220(74), 219(35), 137(11), 136(100), 120(49), 119(42), 118(8), 94(33), 93(75), 83(29), 80(17), 67(9).	[103,104]
130	9-Latifolylretronecine	-	311	312(M ⁺ +1, 40), 195(40), 161(20), 119(100).	[101]
131	Lepanthine	-	315	MS ² : 298, 156, 138, 120, 94.	[166,167]
132	Lindelofine (or stereoisomer)	2678*	285	285(5), 267(5), 252(6), 242(1), 241(1), 240(1), 226(1), 142(30), 125(21), 124(100), 83(26), 82(15), 55(30).	[42]
133	Lithosenine	-	415	415(0.2), 400(10), 297(8), 256(3), 238(100), 237(15), 222(16), 220(24), 138(30), 137(8), 136(49), 121(36), 120(75), 119(36), 95(9), 94(34), 93(57), 80(12)	[156]
134	Longitubine	-	353	353(29), 293(12), 181(29), 180(78), 136(75), 120(69), 119(62), 118(15), 106(10), 101(22), 94(58), 93(100), 80(32), 67(17).	[104]
135	Lycopsamine	2145	299	299(0.5), 254(1), 156(8), 139(31), 138 (100), 137(12), 136(12), 120(10), 108(4), 95(15), 94 (55), 93(84), 80(14), 67(10), 45(8), 43(20).	[91]
136	Macrophylline	-	239	98, 83(100), 55.	[62]
137	Megalanthonine	-	301	301(2), 283(2), 256(11), 240(8), 212(19), 158(86), 141(15), 140(43), 138(14), 124(10), 122(18), 114(13), 97(18), 96(44), 95(62), 83(15), 82(100), 55(32).	[134]
138	1-Methylene-8 α -pyrrolizidine	1274	139	139(15), 95(100).	[205]
139	7-(2-Methylbutyryl)retronecine	1760	239	239(20), 222(2), 154(20), 138(12), 137(12), 136(28), 124(37), 120(20), 111(28), 108(15), 106(28), 94(30), 93(20), 80 (100), 68(10), 57(19).	[96]
140	9-(2-Methylbutyryl)retronecine	1795	239	239(2), 195(5), 154(3), 138(98), 137(8), 136(5), 120(6), 108(5), 94(60), 93(100), 80 (27), 67(15), 57(30).	[96]
141	7-(2-Methylbutyryl)-9-(2,3-dihydroxybutyryl)retronecine	2285	341	341(1), 239(10), 223(20), 222(100), 143(18), 138(11), 137(7), 136(50), 121(17), 120(80), 119(30), 106(8), 94(40), 93(83), 85(15), 80(15), 57(30), 45(9).	[91]
142	7-(2-Methylbutyryl)-9-echimidinyl retronecine	2512	399	399(0.1), 384(0.5), 354(0.5), 297(1), 223(20), 222(100), 221(5), 143(15), 138(8), 137(8), 136(40), 121(30), 120(95), 119(30), 106(9), 94(31), 93 (70), 85(15), 80(15), 67(8), 59(15), 57(28), 45(8), 43(24).	[91]
143	Monocrotaline	2268	325	236(35), 136(46), 120(100), 119(64), 93(36), 80(12), 43(69).	[195]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
144	Myoscorpine	3212*	381	381(0.2), 338(1), 337(2), 336(2), 281(2), 255(1), 238(9), 237(3), 221(33), 220(100), 141(22), 138(8), 136(46), 121(34), 120(71), 119(22), 106(8), 94(36), 93(55), 83(39), 80(19), 59(4), 55(42), 53(11).	[42]
145	Neolatifoline	-	393	393(7), 293(11), 221(16), 220(85), 219(31), 137(13), 136(100), 120(43), 119(48), 118(15), 94(39), 93(79), 83(32), 80(16), 67(8).	[104]
146	(7 <i>S</i> ,8 <i>R</i>)Petranine	-	285	ESIMS (positive mode) <i>m/z</i> 286.11966	[89]
147	(7 <i>S</i> ,8 <i>S</i>)Petranine	-	285	ESIMS (positive mode) <i>m/z</i> 286.12162	[89]
148	Platynecine	-	157	113(18), 82(100), 68(18), 67(4), 55(27).	[106]
149	Platynecine N-Oxide 2 <i>S</i> -hydroxy-2 <i>S</i> (1 <i>S</i> -hydroxyethyl)-4-methyl-pentanosyl ester	-	331	314, 288, 174, 156, 112.	[50]
150	Pycnanthine	2793	397	397(0.8), 382(0.4), 354(2), 352(2), 281(3), 254(12), 237(32), 236(100), 235(7), 138(26), 137(14), 136(74), 121(46), 120(77), 119(20), 99(20), 94(50), 93(58), 80(20), 71(20), 58(15), 45(20), 44(22), 43(20).	[91]
151	Punctanecine	-	383	383(0.2), 368(0.5), 338(3), 296(2), 283(3), 266(4), 240(25), 222(19), 155(13), 140(45), 139(40), 137(73), 123(25), 122(48), 120(14), 96(23), 95(26), 83(27), 82(100).	[169,206]
152	Retronecine	1430 2190*	155	155(26), 138(2), 111(55), 94(15), 80(100), 68(15).	[40]
153	Retronecine dibenzoate	2785	363	363(0), 258(10), 241(20), 136(43), 119(55), 105(100), 94(60), 93(78), 77(35).	[207]
154	Retronecine 2 <i>S</i> -hydroxy-2 <i>S</i> (1 <i>S</i> -hydroxyethyl)-4-methyl-pentanosyl ester	-	313	MS ² : 396, 270, 224, 156, 138.	[50]
155	Retronecine 2 <i>S</i> -hydroxy-2 <i>S</i> (1 <i>S</i> -hydroxyethyl)-[1' <i>S</i> -hydroxyethyl]-4-methylpentanoyl]-4-methyl-pentanoyl ester,	-	471	ESIMS: <i>m/z</i> 472 [M + H] ⁺ , for C ₂₄ H ₄₁ NO ₈	[51]
156	Rinderine	2155	299	284(0.1), 254(0.6), 156(9), 139(35), 138(100), 137(10), 136(10), 120(5), 95 (12), 94(23), 93(70), 80(12), 67(7), 53(5), 43(16).	[70]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
157	Scorpioidine	-	381	381(7), 199(7), 139(11), 138(69), 137(28), 136(13), 120(9), 101(8), 95(4), 94(21), 93(41), 83(100), 80(9), 67(6), 57(6), 55(34), 53(6), 43(10).	[159]
158	7-Seneciойhelotridine	1870	237	137(35), 136(18), 124(20), 111(35), 106(90), 94(21), 83(15), 80(100), 68(8), 55(18).	[70]
159	7-Seneciойlretronecine	1816	237	237(4), 154(4), 137(30), 136(16), 124(25), 111(37), 106(40), 94(21), 83(23), 80(100), 68 (8), 55(15).	[91]
160	9-Seneciойlretronecine	1833	237	237(1), 193(2), 155(11), 154(10), 138(23), 137(28), 136(15), 126(9), 109(5), 94(25), 93(100), 83(20), 80(16), 67(6), 55(11).	[91]
161	7-Seneciойlrinderine	2515	381	336(0.1), 221(28), 220(61), 138(10), 137(15), 136(50), 121(75), 120(100), 119(85), 106(23), 95(15), 94(48), 93(72), 83(27), 80(30), 55(40), 43(40).	[40]
162	7-Seneciойllycopsamine	2497	381	336(0.5), 281(1), 238(5), 221(28), 220(100), 219(4), 141(15), 138(14), 137(12), 136(80), 121(38), 120(70), 119(20), 94(38), 93(61), 83 (76), 80(11), 55(15), 45(8), 43(28).	[91]
163	Sincamidine	-	313	C ₁₆ H ₂₇ NO ₅ (similar to heliotrine)	[44]
164	Senkirkine	2460	365	365(1), 266(10), 250(6), 222(9), 168(24), 153(41), 80(38), 43(100).	[54,195]
165	Subulacine	-	155	155(17), 126(4), 124(13), 96(10), 80(4), 71(5), 70(100), 68(10), 56(6), 55(65).	[106,208]
166	Supinine	1978	283	283(0.2), 140(6), 123(25), 122(100), 121(40), 120(49), 108(11), 93(20), 80(8), 70(7), 53(5), 45(4), 43(12).	[70]
167	Supinidine	1887*	139	139(40), 138(12), 122(32), 120(14), 111(15), 110(18), 108(30), 94(13), 80(100), 70(4), 68(17), 55(14), 53(17).	[42]
168	Supinidine N-oxide 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester	-	313	MS ² : 296, 270, 224, 156, 138.	[50]
169	Symlandine	3194*	381	381(0.3), 338(1), 337(2), 336(2), 281(2), 255(1), 238(9), 237(3), 221(30), 220(100), 141(19), 138(10), 136(47), 121(35), 120(72), 119(21), 106(9), 94(36), 93(52), 83(31), 80(17), 59(3), 55(40), 53(12).	[42]
170	Symphytine	3240*	381	381(0.4), 338(1), 337(1), 336(3), 281(2), 255(1), 238(9), 237(2), 221(33), 220(100), 141(21), 138(7), 136(44), 121(33), 120(70), 119(20), 106(7), 94(36), 93(52), 83(33), 80(18), 59(3), 55(38), 53(12).	[42]
171	Symviridine	-	381	381(0.3), 337(0.1), 336(0.1), 281(0.2), 221(34.5), 220(100), 136(44.2), 121(22), 120(50), 119(11), 118(15), 117(7.6), 103(10), 95(23.5), 93(44.5).	[172]

Table 3. Cont.

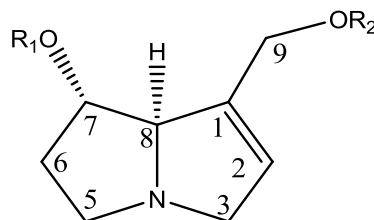
No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
172	Tessellatine	2930*	299	299(7), 281(7), 256(5), 255(3), 248(4), 238(11), 237(9), 236(11), 156(19), 139(25), 138(64), 137(23), 124(16), 120(40), 111(45), 108(29), 106(39), 94(54), 93(40), 80(100), 53(17).	[42]
173	7-Tigloyl-9-(2,3-dihydroxybutyryl)retronecine	2325	339	239(5), 238(5), 237(8), 221(22), 220(90), 219 (20), 141(20), 138(10), 137(11), 136(100), 121(15), 120(80), 119(35), 106(10), 94(58), 93(90), 83(46), 80(20), 75(2), 57(9), 55(40), 45(10).	[96]
174	7-Tigloyl-9-(2,3-dihydroxypropanoyl)retronecine	2320	325	237(8), 225(12), 221(12), 220(70), 141(27), 138(5), 137(12), 136(93), 121(8), 120(55), 119(48), 106(10), 94(59), 93(100), 83(55), 80(18), 55(24).	[40]
175	7-Tigloylheliotridine	1873	237	237(0.5), 137(55), 136(15), 124(19), 120(5), 111(41), 107(10), 106(100), 94(20), 86(6), 83(12), 80(95), 68(5), 55(19).	[67]
176	7-Tigloyl-9-(hydroxypropenoyl) retronecine	2073	307	221(14), 220(100), 207(27), 181(10), 141(42), 137(10), 136(95), 120(53), 119(28), 106(10), 94(63), 93(84), 83 (50), 80(20), 67(9), 55(37), 43(24).	[40]
177	7-Tigloyllycopsamine	2473*	381	336(1), 281(1.5), 238(1), 221(20), 220(100), 136(60), 121(30), 120(80), 94(40), 93(70), 83(50), 80(18), 55(40).	[90]
178	7-Tigloyl-9-(2-methylbutyryl)retronecine	2170	321	221(36), 220(100), 195(5), 141(32), 138(2), 137(10), 136(82), 121(6), 120(53), 119(25), 106(10), 94(53), 93(80), 83(40), 80(15), 57(20), 55(33).	[96]
179	7-Tigloylretronecine	1816	237	237(3), 219 (0.5), 154(2), 138(3), 137(29), 136 (15), 124(25), 120(5), 111(44), 106(50), 94(20), 93(6), 83(15), 80 (100), 55(22).	[96]
180	9-Tigloylretronecine	1843	237	193(5), 154(15), 138(20), 137(26), 136(13), 126(7), 119(5), 109(4), 94(23), 93(100), 83(10), 80(12), 55(18).	[96]
181	Trachelanthamidine	1853*	141	141(24), 140(10), 124(15), 110(9), 108(7), 83(100), 82(62), 70(8), 68(8), 55(45).	[42]
182	Trachelanthamine	1970	285	267(5), 252(4), 240(4), 142(50), 125 (18), 124(100), 110(4), 96(6), 83(20), 82(11), 70(6), 55(14), 43(12).	[70]
183	Trachelanthamidine 2S-hydroxy-2S(1S-hydroxyethyl)-4-methyl-pentanoyl ester	-	299	ESIMS: <i>m/z</i> 300 [M + H] ⁺ , 142, 89, 83, 82, 55.	[51]
184	7-Trachelanthyl retronecine	2899*	299	299(12), 281(6), 236(11), 156(25), 138(50), 120(47), 111(45), 108(29), 106(40), 94(40), 93(320), 80(100).	[42]
185	Transalpinecine	-	173	98, 83, 70.	[145]

Table 3. Cont.

No.	Alkaloid	RI	[M] ⁺	Characteristic ions <i>m/z</i> (relative abundance)	References
186	Triangularine	2375	335	237(23), 236(6), 235(4), 221(5), 220(30), 219(18), 141(12), 137(12), 136(100), 121(28), 120(64), 119(35), 95(12), 94(60), 93(98), 83(58), 80(15), 55(30).	[40]
187	Triangularicine	2394	335	237(30), 236 (6), 235(3), 221(5), 220(31), 219(10), 141(18), 137(10), 136(83), 121(27), 120(51), 119(40), 95(10), 94(55), 93(100), 83(60), 80(15), 55(25).	[40]
188	Trichodesmine	2388	353	353(1), 264(56), 222(5), 136(36), 120(100), 93(23), 81(16), 43(40).	[195]
189	Turneforcidine	-	157	113(20), 82(100), 68(21), 67(6), 55(32).	[106]
190	Uluganine		399	399(2), 384(8), 356(1), 355(3), 354(2).	[183]
191	Uplandicine	2337	357	357(4), 342(5), 297(23), 281(4), 256(4), 207 (7), 206(52), 181(80), 180 (100), 179 (43), 136(75), 121(49), 120(85), 119 (50), 101(23), 94(55), 93(74), 80(28), 73(74), 59(23), 45(20), 44(69), 43(48).	[163]
192	Viridinatine	-	443	282(17), 138(41), 137(86), 124(32), 111(70), 106(42), 94(44), 80(100).	[76,187]
193	Viridiflorine	1983	285	284(0.3), 267(5), 252(5), 240(5), 142 (70), 125 (23), 124 (100), 117(3), 110 (5), 83 (35), 82 (22), 70 (15), 55(25), 43(21).	[67]
194	9-Viridifloryl turneforcidine (or isomer)	2394*	301	301(0.3), 283(8), 257(8), 256(14), 212(18), 159(21), 158(68), 141(17), 140(50), 138(32), 122(24), 121(12), 120(31), 117(10), 106(13), 96(43), 95(81), 83(20), 82(100), 69(22), 55(40).	[42]
195	Vulgarine	-	397	398[M+ 1] ⁺ , 380(18), 336(5), 316(5), 298(40), 254(15), 240(52), 138(100), 120(14).	[11]

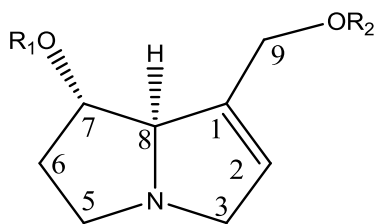
The RI reported for DB1 capillary column; * RI for DB-1701 capillary column; ** RI for OV1 capillary column; - not determined.

Figure 16. Pyrrolizidine alkaloid structures in Boraginaceae. Compounds are numbered as in Table 3.



R1	R2	
H	H	Heliotridine (112)
Ang	H	7-Angeloylheliotridine (46)
Tigl	H	7-Tigloylheliotridine (175)
Sen	H	7-Seneciroylheliotridine (158)
Ac	Cura	7-Acetyl-9-curassavoylheliotridine (3)
H	Cura	9-Curassavoylheliotridine (66)
H	(-)-Vir	Echinatine (82)
Ang	(-)-Vir	7-Angeloylechinatine (45)
Ac	(-)-Vir	7-Acetylechinatine (7)
H	(-)-Vir,3'-OAc	3'-Acetylechinatine (6)
H	(+)-Vir	Isoechinatine (122)
H	Heliot	Heliotrine (114)
Ang	Heliot	7-Angeloyheliotrine (47)
H	(+)-Trcah	Rinderine (156)
Ac	(+)-Trach	7-Acetylreinderine
H	(+)-Trach,3'-OAc	3'-Acetylreinderine (25)
Ang	(+)-Trcah	7-Angeloylrinderine (54)
Sen	(+)-Trach	7-Seneciroylrinderine (161)
Ang	Ang	Asperumine (56)
Ang	Ech	Heliosupine (111)
Ang	Ech, 3'-OAc	3'-Acetylheliosupine (13)
H	Las	Europine (91)
H	Las,5'-OAc	5'-Acetyeuropine (10)
Ac	Las	7-Acetyeuropine (11)
Ang	Las	Lasiocarpine (128)
Ang	Las,5'-OAc	5'-Acetyllasiocarpine (18)
Ang	Las,2'-OAc	2'-Acetyllasiocarpine
Ang	5'-Deoxy Las	5'-Deoxylasiocarpine (70)
(-)-Vir	(-)-Vir	Viridinate (192)
H	(-)-Lact	Lactodine (127)
H	Vir or Trach, 3'-O- <i>p</i> -hydroxycinammoyl	Cynoglossamine (69)
3-Hydroxy-3-MeBut	(+)-Trach, 5'-OH	Canescine (58)

Figure 16. Cont.

**R1**

3-Hydroxy-3-MeBut

3-Hydroxy-3-MeBut

3-Hydroxy-3-MeBut

Ang

Ang

3-Hydroxy-3-methyl butanoic acid

Tigl

H

R2

(+) -Trach, 5'-OH-3'-OAc

(-) -Vir, 5'-OH

(+) -Vir, 5'-OH-3'-OAc

2,3-DiHydBut

2-MeBut

Vir. or its isomer Trach.

(2-deoxy-2-methyl) Ech.

2,3-dimethyl-2,3,4-trihydroxypentanoic

3'-Acetylcanescine (1)

Canescenine (59)

3'-Acetylcasescenine (2)

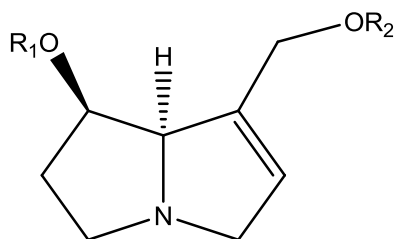
7-Angeloy-9-(2,3-dihydroxybutyryl)heliotridine (40)

7-Angeloyl-9-(2-methylbutyryl)heliotridine (49)

Uluganine (190)

7-Tigloyl-9-(2-deoxy-2-methyl)echimidinyl heliotridine.

Onosmectine

**R1**

H

Ac

Ac

Ang

H

Sen

H

Tigl

H

Trach

H

H

Ac

R2

H

H

t Sarr

H

Ang

H

Sen

H

Tigl

H

(+) -Trach

(+) -Trach, 3'-OAc

(+) -Trach

Retronecine (152)

7-Acetylretronecine (24)

7-Acetyl-9-sarracinyltretronecine (26)

7-Angeloyltretronecine (51)

9-Angeloyltretronecine (52)

7-Seneciolyltretronecine (159)

9-Seneciolyltretronecine (160)

7-Tigloyltretronecine (179)

9-Tigloyltretronecine (180)

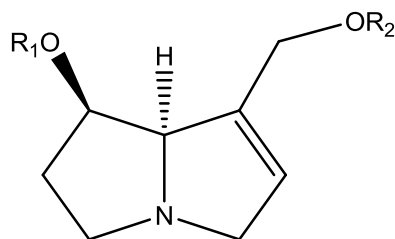
7-Trachelanthylretronecine (184)

Intermedine (126)

3'-Acetylintermedine (16)

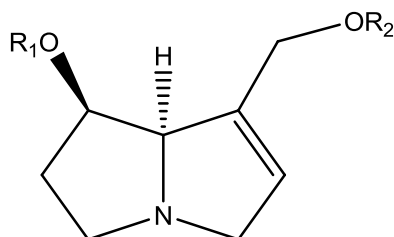
7-Acetylintermedine (17)

Figure 16. Cont.



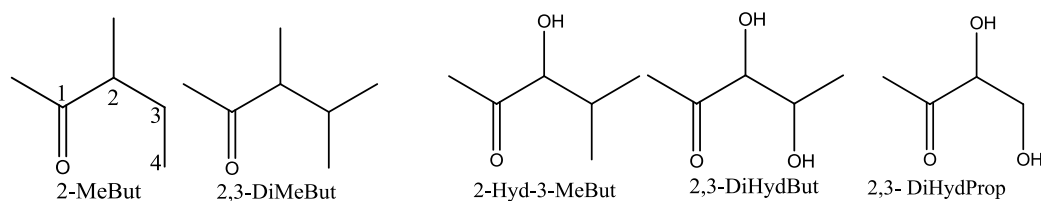
R₁	R₂	
Ac	(+)-Trach,3'-OAc	3',7-Diacetylintermedine (71)
Ac	(-)-Vir,3'-OAc	3',7-Diacetyllycopsamine (72)
H	(-)-Vir	Lycopsamine (135)
H	(-)-Vir,3'-OAc	3'-Acetyllycopsamine (20)
Ac	(-)-Vir	7-Acetyllycopsamine (21)
Ang	(-)-Vir	7-Angeloyllycopsamine (48)
Sen	(-)-Vir	7-Senecioyllycopsamine (162)
Tigl	(-)-Vir	7-Tigloyllycopsamine (177)
H	(-)-Trach	Indicine (121)
Ac	(-)-Trach	7-Acetylindicine
H	(-)-Trach,3'-OAc	3'-Acetylindicine (15)
Tigl	(+)-Trach	Myoscorpine (144)
Tigl	(+)-Trach,3'-OAc	3'-Acetylmyoscorpine (23)
Tigl	(+)-Trach,5'-OH	Hydroxymyoscorpine (117)
Ang	(+)-Trach	Echiumine (83)
Ang	(+)-Trach,3'-OAc	3'-Acetylechiumine (8)
threo-2'',3''-dihydroxy Ang	(+)-Trach	threo-2'',3''-Dihydroxyechiumine (76)
2'',3''-epoxy Ang.	(+)-Trach	2'',3''-Epoxyechiumine (88)
erythro-3''-chloro-2''-hydroxy	(+)-Trach	erythro-3''-Chloro-2''-hydroxyechiumine (89)
Ang		
Sen	(+)-Trach	Echiupinine (85)
Ang	Ech	Echimidine (80)
Tigl	Ech	Echimidine isomer (tigloyl) (81)
Ang	Ech,3'-OAc	3'-Acetylechimidine (9)
Ang	Ech,5'-OAc	5'-Acetylechimidine
H	Ech.	Echimiplatine
Sen	Ech	Echihumiline (79)
Sen-4-OH	(+)-Trach	Pcynanthine (150)
Ang	t Sar	Triangularine (186)
Tigl	t Sar	Triangularicine (187)
Ang	(-)-Vir	Symlandine (169)
Tigl	(-)-Vir	Symphytine (170)
Sen	(-)-Vir	Symviridine (171)
(+)-Vir	H	iso-Lycopsamine (123)

Figure 16. Cont.



R₁	R₂	
(-)-Vir	H	Heliospathuline (110)
(-)-Vir	H	Tessellatine (172)
(-)-Vir,3'-OAc	H	3'-Acetyltessellatine (29)
(-)-Vir	Ac	9-Acetyltessellatine (30)
(-)-Vir,3'-OAc	Ac	3',9-Diacetyltessellatine (73)
H	(-)-Curss	Heliospathine (109)
H	Vir,3'-OAc	9-(3'-Acetyl)viridifloryl retronecine (34)
H	Helio	Sincamidine (163)
Ang	Latif	Latifoline (129)
Ang	Latif isomer	Neolatifoline (145)
H	Latif	9-Latifolylretronecine (130)
H	Hacke	Hackelidine
Ac	Latif.	Longitubine (134)
H	(+)-Trach,3'-OTigl	Anadoline (38)
H	(-)-Vir,3'-OTigl	Scorpioidine (157)
Ac	(-)-Vir,3'-OTigl	7-Acetylscorpioidine (27)
H	(+)-Trach, 5'-OH	Leptanthine (131)
H	(+)-Trach, 5'-OAng	Vulgarine (195)
Ac	(+)-Trach, 5'-OAng	7-Acetylvulgarine (36)
Ang	(+)-Trach, 5'-OAng	Echivulgarine (86)
Ac	(+)-Trach, 5'-OH	Uplandicine (191)
H	Vir,3'-OiVal	9-(3'-Isovaleryl)viridifloryl retronecine (125)
Vir	H	7-Viridiflorylretronecine
3-Hydroxy-3-MeBut	(+)-Vir,5'-OH-3'-OAc	3'-Acetyllithosenine (19)
2-MeBut	(+)-Trach	Furcatine (96)
2-MeBut	(+)-Trach,3'-OAc	3'-Acetylfurcatine (12)
3-Hydroxy-3-MeBut	(-)-Vir,5'-OH	Lithosenine (133)
Benz	Benz	Retronecine dibenzoate (153)
2-Me-2,3-dihydroxy-But	Ang	Cryptanthine (62)

Figure 16. Cont.



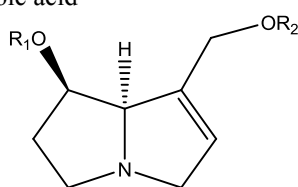
2-MeBut = 2-Methylbutric acid

2,3-DiMeBut = 2,3-Dimethylbutric acid

2-Hyd-3-MeBut = 2-Hydroxy-3-methylbutric acid

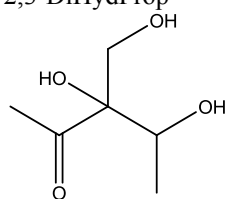
2,3-DiHdBut = 2,3-Dihydroxybutric acid

2,3-DiHdProp = 2,3-Dihydroxypropanoic acid



R₁	R₂	
2-MeBut	H	7-(2-Methylbutyryl)retronecine (139)
H	2-MeBut	9-(2-Methylbutyryl)retronecine (140)
2-MeBut	2,3-DiHdBut	7-(2-Methylbutyryl)-9-(2,3-dihydroxybutyryl)retronecine (141)
2-MeBut	Ech	7-(2-Methylbutyryl)-9-echimidinyl retronecine (142)
Ang	2-MeBut	7-Angeloyl-9-(2-methylbutyryl)retronecine (50)
Vir	Ang	9-Angeloyl-7-viridifloryl retronecine (55)
Tigl	2-MeBut	7-Tigloyl-9-(2-methylbutyryl)retronecine (178)
Ang	2-Hyd-3MeBut	7-Angeloyl-9-(2-hydroxy-3-methylbutyryl)retronecine
Tigl	2-Hyd-3MeBut	7-Tigloyl-9-(2-hydroxy-3-methylbutyryl)retronecine
Ang	2,3-DiHdBut	7-Angeloyl-9-(2,3-dihydroxybutyryl)retronecine (41)
Tigl	2,3-DiHdBut	7-Tigloyl-9-(2,3-dihydroxybutyryl)retronecine (173)
Ac	2-MeBut	7-Acetyl-9-(2-methylbutyryl)retronecine (22)
Ac	2,3-DiMeBut	7-Acetyl-9-(2,3-dimethylbutyryl)retronecine (5)
Ac	2-Hy-3MeBut	7-Acetyl-9-(2-hydroxy-3-methylbutyryl)retronecine (14)
Ac	2,3-DiHdBut	7-Acetyl-9-(2,3-dihydroxybutyryl)retronecine (4)
Ang	2,3-DiHdProp	7-Angloyl-9-(2,3-dihydroxypropanoyl)retronecine (42)
Tigl	2,3-DiHdProp	7-Tigloyl-9-(2,3-dihydroxypropanoyl)retronecine (174)

Ang

Dihydroxytriangularine (**77**)

Tigl

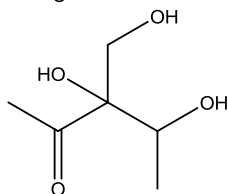
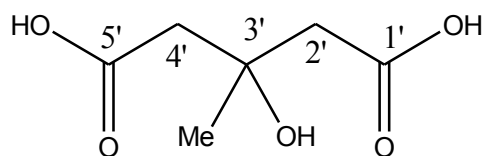
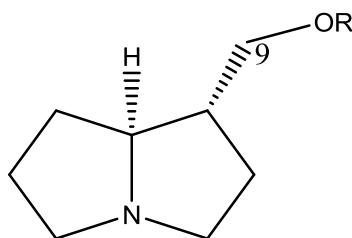
Dihydroxytriangularicine (**78**)

Figure 16. Cont.



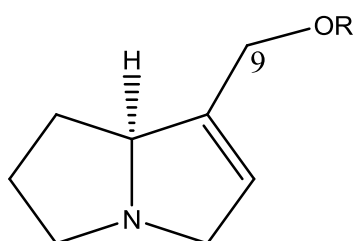
3-hydroxy-3-methylglutaric acid

R₁	R₂	
Ang	3-hydroxy-3-methylglutaric acid	Echiuplatine (84)
Ang	3-hydroxy-3-methylglutaric acid methyl ester	Methylechiuplatine



R	
H	(-)-Trachelanthamidine (181)
Ac	9-Acetyltrachelanthamidine (32)
Ang	9-Angeloyltrachelanthamidine (54)
(+)-Trach	Trachelanthamine (182)
(+)-Trach,3'-OAc	3'-Acetyltrachelanthamine (31)
(+)-Vir	Coromandaline (60)
(-)-Curass	Curassavine (64)
(-)-Vir,5'-OH	Floridimine (93)
(-)-Vir,5'-OH-3'-OAc	Floridine (94)
(-)-Trach,5'-hydroxyl	Floridinine (95)
(-)-Trach	Heliovicine (115)
(-)-Vir	Viridiflorine (193)
(-)-Vir,3'-OAc	3'-Acetylviridiflorine (33)
(2R,3R)-2,3-Dihydroxy-3-methylpentanoyl	Strigosine
Ech	Macrotomine

Figure 16. Cont.



R

H

(+) -Trach, 3'-OAc

(-) -Vir

(+) -Vir

(-) -Curass

Heliot

Las

(+) -Trach

(-) -Supinidine (167)

3'-Acetylsupinine (28)

Amabiline (37)

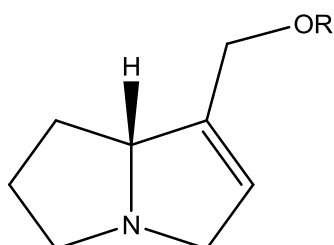
Coromandalinine (61)

Curassavinine (65)

Heleurine (97)

Ilamine (119)

Supinine (166)



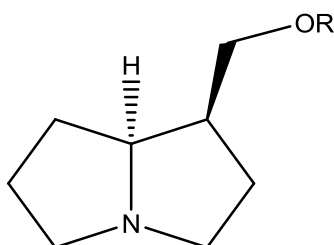
R

H

(-) -Vir

(+) -Supinidine (167)

Cynaustine (67)



R

H

(+) -Vir

(-) -Curass

(-) -Trach

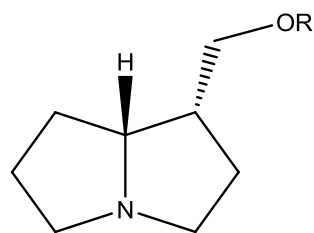
(-) -Isoretronecanol (124)

Heliocoromandaline (105)

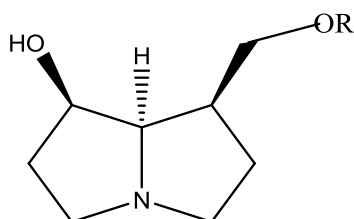
Heliocurassavine (106)

Heliocurassavicine (107)

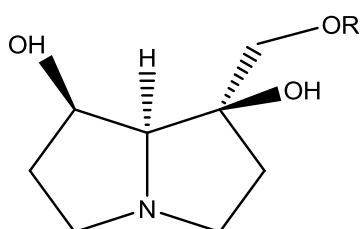
Figure 16. Cont.



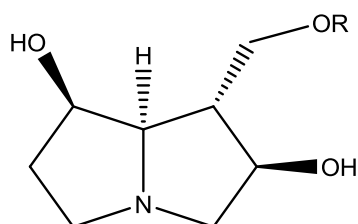
R	
H	(+)-Isoretronecanol [(+)-Lindelofidine] (124)
(-)-Vir	Cynaustraline (68)
(+)-Trach	Lindelofine (132)
(+)-Trach, 3'-OTigl	Lindelofamine
<i>p</i> -Hydroxycinnamoyl	Thesinine
4'- <i>p</i> -Hydroxy-cinnamoylglucoside	Thesinine-4'-O- β -D-glucose



R	
H	Platyneceine (148)
(-)-Vir	Megalanthoine (137)

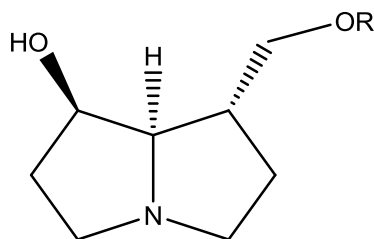


R	
H	Helibractinecine (99)
Ang	Heliscabine (116)

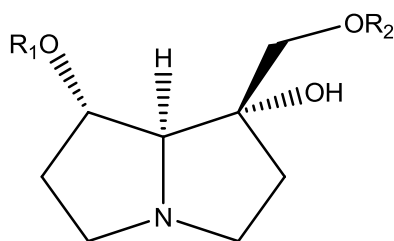


R	
H	Helifolinecine or croalbinecine (103)
Ang	Helifoline (102)

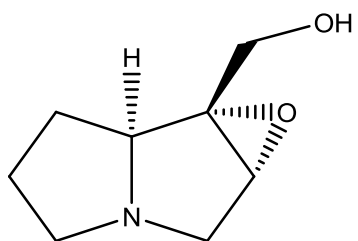
Figure 16. Cont.



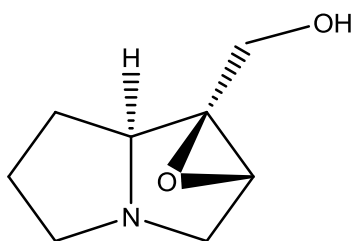
- | | |
|-------------|--|
| R | |
| H | (-) Turneforcidine (189) |
| Vir, 3'-OAc | 9-(3'-Acetyl)viridifloryl turneforcidine (35) |
| Vir | 9-Viridifloryl turneforcidine (194) |



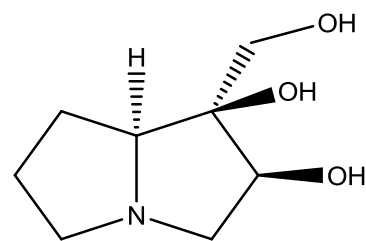
- | | | |
|-----------|-----------|------------------------------------|
| R1 | R2 | |
| H | H | Helibracteatinecine (100) |
| H | Ang | Helibracteatine (98) |
| Ang | H | Helibracteatinine (101) |



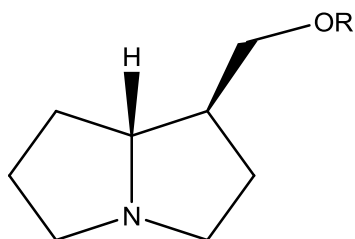
1α,2α-Epoxy-1β-hydroxymethyl-8α-pyrrolizidine (**90**)



Subulacine (**165**)

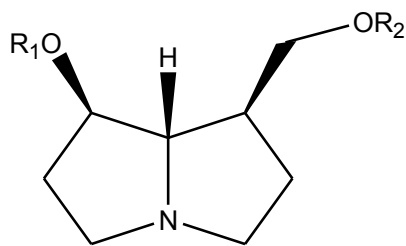


Transalpinecine (**185**)



- | | |
|-----------|---|
| R | |
| H | Laburnine [(+)-trachelanthamidine] (181) |
| (-)-Trach | Heliocurassavinine (108) |
| (-)-Vir | Neocormandaline |
| (+)-Trach | 9-(+)-Trachelanthyl laburnine |

Figure 16. Cont.



R1

H

Ang

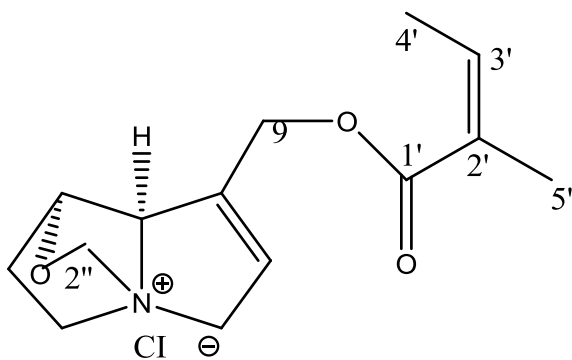
R2

H

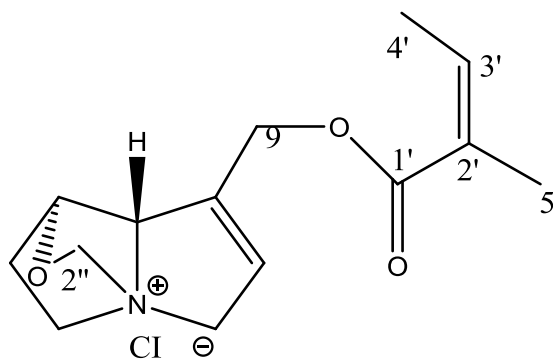
(-)-Vir

(+)-Hastanecine

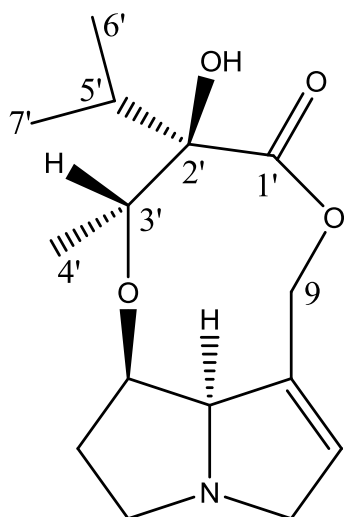
Punctanecine (151)



(7S, 8R)-Petranine (146)



(7S, 8S)-Petranine (147)



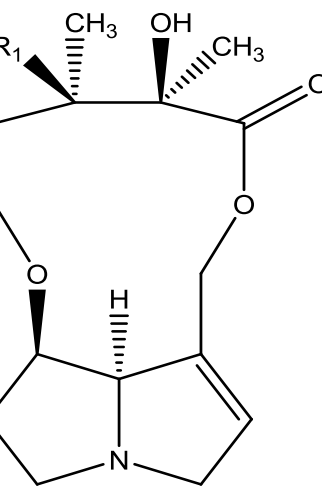
Helindicine (104)

R1

H

OH

OH



R2

CH(CH₃)₂

CH₃

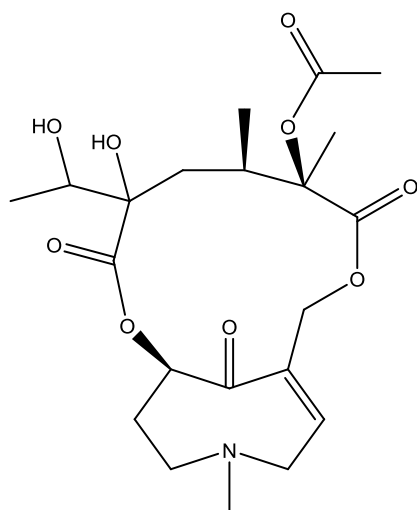
CH(CH₃)₂

Incanine (120)

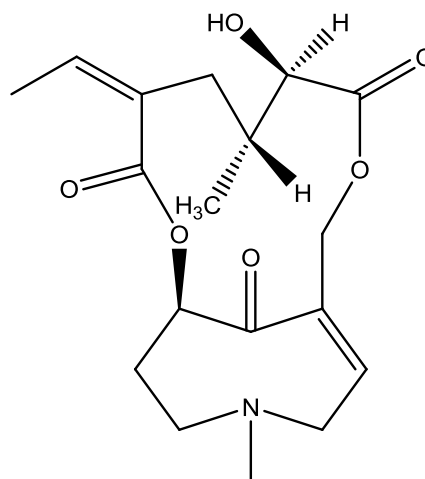
Monocrotaline (143)

Trichodesmine (188)

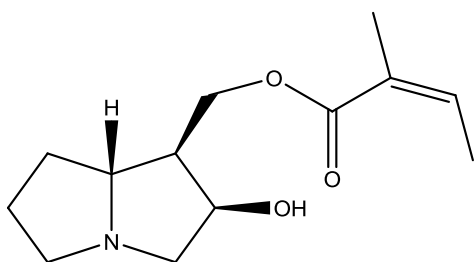
Figure 16. Cont.



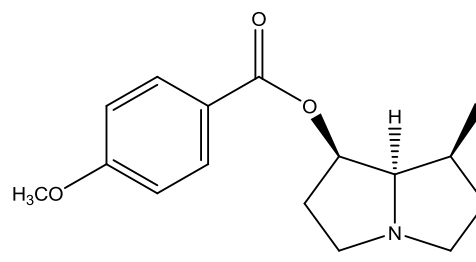
Floridanine (92)



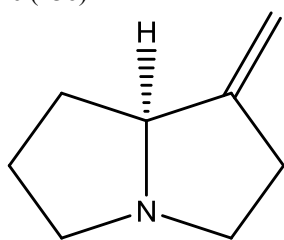
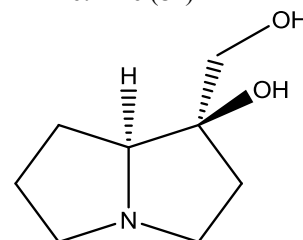
Senkirikine (164)



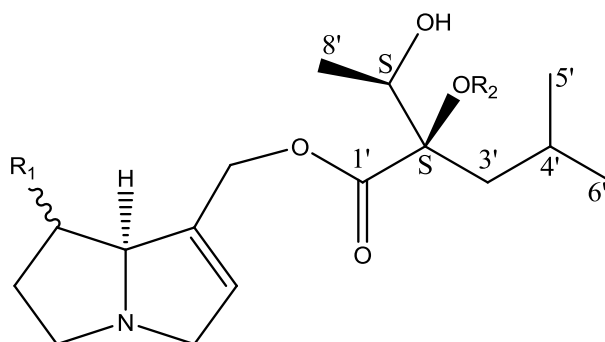
Macrophylline (136)



Ehretinine (87)

1-Methylene-8 α -pyrrolizidine (138)

Curassanecine (63)



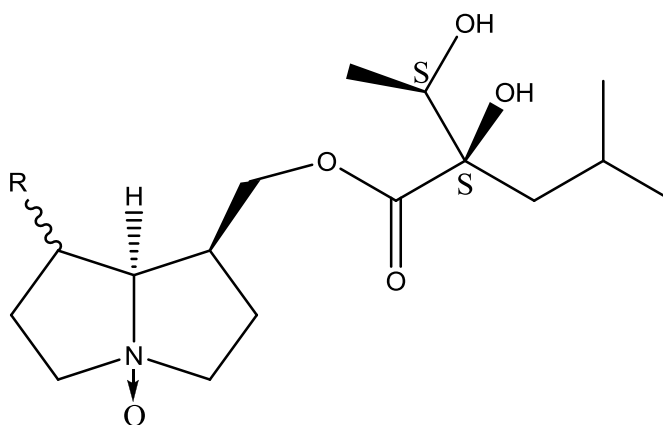
$R_1 = \text{-----} \text{OH}$, $R_2 = \text{H}$: Heliotridine 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester (113)


$R_1 = \text{▀} \text{OH}$, $R_2 = \text{H}$: Retronecine 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester (154)

$R_1 = \text{▀} \text{OH}$, $R_2 = \text{Erythro-2-hydroxy-2-(1-hydroxyethyl)-4-methyl-pentanol}$: Retronecine 2S-hydroxy-2S-(1S-hydroxyethyl)-2S-[1'S-hydroxyethyl)-4-methyl-pentanoyl]-4-methyl-pentanoyl ester (155)

$R_1 = \text{H}$, $R_2 = \text{H}$: Supinidine N-Oxide 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester (168)

Figure 16. Cont.



R =  OH, Platynecine N-Oxide 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester (**149**)

R = H: Trachelanthamidine 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester (**183**)

2.1.1. Gas Liquid Chromatography-Mass Spectrometry (GLC-MS)

High resolution Gas-liquid chromatography coupled with mass spectrometry (GLC-MS) has become a valuable and highly sensitive means for separation, convenient identification and quantification of complex PA mixtures, even in minute quantities or in diastereoisomeric forms [40,59,67,70,90,91,96,163,191–195]. The combination of molecular weight, group mass fragmentation pattern and Kovats retention indices, enables an unequivocal identification of most of PA tertiary bases even in trace amounts or of closely related isomers. High resolution gas chromatography-mass spectrometry (HRGC-MS) using the SIM mode was applied to detect trace amounts of 1,2-unsaturated PAs in 55 commercially available pollen products [16]. The detection limit of the overall procedure and the reliable quantitation limit were $0.003 \mu\text{g g}^{-1}$ to $0.01 \mu\text{g g}^{-1}$. GLC and GLC-MS cannot detect N-oxides, because they are not volatile. PA N-oxides need to be reduced to the free base (for example by reduction with zinc in HCl) as an extra step in the sample preparation to make them suitable for GLC analysis.

2.1.2. Liquid Chromatography-Mass Spectrometry (LC-MS)

Coupling of liquid chromatography (LC) with mass spectrometry (MS) allows a simultaneous determination of PAs and their corresponding N-oxides in a single chromatographic run without the requirement of a reduction step [50]. Quantitative analysis of PA mixtures (e.g., from comfrey, *Symphytum officinale*) was carried out efficiently using electrospray liquid chromatography-mass spectrometry (LC-MS). The method is based on HPLC coupled to an ion-trap and orbitrap MS with electrospray ionization interface [177]. Plant samples from 9 Boraginaceous species have been screened with gradient HPLC equipped with diode array and electron impact mass spectrometry [60]. Several saturated and 1,2-unsaturated PAs (mainly as N-oxides) were detected using HPLC-ESI-MS in fresh pollen collected from flowers of the PAs producing plants *Echium vulgare* and *E. plantagineum* and /or from bee pollen from bees that had foraged on PA plants [12]. The same method has also been used to determine the PA profile in *E. plantagineum* [93], *Cryptantha crassipes* [64], and *Anchusa strigosa* [50]. PAs (N-oxides and free bases) occurring in small amounts could be efficiently analyzed using an RP-HPLC ion trap MS method with an atmospheric pressure chemical ionization (APCA) interface [167].

Most PAs in plants are present as N-oxides or their tertiary bases. The N-oxides of this class are polar, water soluble, non-volatile and thermally labile. Thus, the application of LC-MS to the analysis of PA N-oxides has become a widely applied method [64,177,199,209,210], for example, in honey samples.

2.2. Nuclear Magnetic Resonance (NMR)

For the determination of the type of necine, the sites of ester attachment and the stereochemical orientation of necic acids, NMR methods are essential. An excellent comprehensive review of ^1H NMR spectral data of PAs (more than 350 compounds) has been published by Logie *et al.* [211], in which the most useful shift values for the different types of PAs have been documented. Roeder [212] reported the ^{13}C NMR data of 136 PAs and updated his data in a book chapter of Rizk [28]. After that time, more NMR data have been published for new PAs which are documented in this review.

2.3. Enzyme-Linked Immunoassay

A highly sensitive and specific competitive enzyme-linked immunosorbent assay (ELISA) can be used for detection and quantification of PAs [213–216]. The limit of detection of this ELISA method was 1.9, 10, 18, 20 and 60 ng for lasiocarpine, lasiocarpine N-oxide, heliotrine, and heliourine N-oxide, respectively [217]. These data suggest that this technique can be an excellent tool to diagnose poisoned animals and identify PA contaminated food items.

3. Tissue Culture

Several Boraginaceae species were subjected to *in vitro* cultivation and their PA contents have been studied [153,218,219]. PA profiles of Hairy root cultures of *Cynoglossum officinale* and *Symphytum officinale* have been established [220]. In these cultures, all PAs are genuinely present as N-oxides. Recently, Abd El-Mawla [221] reported the influence of methyl jasmonate, quercetin and salicylic acid as elicitors of PA production in the hairy root cultures of *Echium rauwolfii*.

4. Variation of PAs between Plant Organs and Developmental Stages

Distributions of PAs vary within different plant organs. In *Heliotropium indicum* a tissue-specific PA analysis revealed the presence of PAs in all tissues: highest levels were detected in the inflorescences which contained more than 70% of total plant alkaloids [116,220]; the alkaloid contents of stems, leaves and roots were 3, 7 and 19%, respectively. Young leaves, young inflorescences or seedlings showed high alkaloid levels, reaching 5%–6% dry matter in *H. spanthulatum* [116]. The total alkaloid contents of the root and rhizome of *Pulmonaria obscura* lay between 0.026 and 0.158 mg/g dry weight, whereas leaves and inflorescences accumulated only trace amounts of PAs (below 0.4 ng/mg dry weight) [168]. Extreme differences were found in PA levels between different leaves of *Cynoglossum officinale* [219]. The youngest leaves of the rosette plants had significantly higher PA contents than the oldest leaves (190 times). Alkaloid profiles and contents (total PAs and free bases) in the different plant organs of *Paracaryum rugulosum*, *P. intermedium*, *Anchusa arvensis*, *Anchusa milleri*, *Alkanna orientalis*, *Alkanna tuberculata*, *Lappula spinocarpos* and *Trichodesma africana* have been reported [40].

Table 4. ^{13}C NMR data of new pyrrolizidine alkaloids (PAs) in the time frame 1991–2013.

Alkaloid	C-1	C-2	C-3	C-5	C-6	C-7	C-8	C-9	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'	C-1''	C-2''	C-3''	C-4''	C-5''	C-6''	solvent	References
Necine Base																							
Helibractinecine	82.8	38.3	53.4	52.5	36.2	73.7	71.2	68.6														CDCl ₃ - CD ₃ OD	[111]
Helibracteatinecine	82.6	34.1	53.0	52.9	33.3	79.7	73.0	67.2														CDCl ₃ - CD ₃ OD	[112]
Turneforcidine	40.8	32.6	56.2	52.8	37.5	72.0	73.7	65.6														CD ₃ OD- ND ₃	[222]
Transalpinecine	82.3	84.4	59.2	55.9	28.0	24.6	72.3	63.9														CD ₃ OD	[145]
Subulacine	70.9	63.4	54.0	58.4	27.1	26.2	67.9	60.2														CD ₃ OD	[145]
1 α -2 α -epoxy-1 β - hydroxymethyl-8 α - pyrrolizidine	83.7	65.2	62.3	56.2	27.9	25.0	72.1	64.0														CD ₃ OD	[145]
Tertiary base and N-oxide alkaloids																							
3'-Acetylcanescine	133.0	127.5	62.6	53.6	34.4	74.4	75.4	62.3	175.1	84.3	72.4- (CO:170.4), (Me: 21.2)	17.2	33.1	17.2	17.1	171.7	46.9	69.1	29.4	29.2		CDCl ₃ /D ₆ - DMSO	[154]
3'-Acetylcanescenine	133.0	127.5	62.6	53.6	34.4	74.4	75.4	62.3	175.1	84.3	73.7- (CO:170.4), (Me: 21.3)	16.0	33.1	17.8	14.2	171.7	46.9	69.1	29.4	29.2		CDCl ₃ /D ₆ - DMSO	[154]
3'-Acetylechihumiline N-oxide	133.0	124.9	79.4	70.5	33.9	73.3	95.6	63.0	174.7	85.6	74.8- (Me: 21.6)	61.1	74.0	27.3	26.4	166.8	116.2	161.9	28.0	21.0		CD ₃ OD	[166]
7-Acetylechinatine N- oxide	133.0	124.3	79.0	70.1	33.4	73.8	95.0	62.1	175.0	85.2	72.4	18.2	34.0	18.5	16.7	171.5	21.1					CD ₃ OD	[69]
7-Acetyleuropine	135.0	128.3	62.3	54.4	30.6	76.9	78.8	62.6	174.2	84.0	79.2- (OMe:56.8)	13.3	73.4	26.7	24.9	171.3	21.5					CDCl ₃	[110]
3'-Acetylcindicine	132.3	130.7	62.8	53.0	36.1	71.1	78.5	63.3	174.5	81.6	71.8- (CO:170.0), (Me 21.1)	14.3	32.3	17.2	16.3							CDCl ₃	[158]

Table 4. Cont.

Alkaloid	C-1	C-2	C-3	C-5	C-6	C-7	C-8	C-9	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'	C-1''	C-2''	C-3''	C-4''	C-5''	C-6''	solvent	References
Tertiary base and N-oxide alkaloids																							
3'-Acetylandicine N-Oxide	132.4	121.9	78.0	69.6	34.7	69.6	95.8	62.1	173.8	81.9	72.4-(CO:170.3), (Me: 21.2)	14.0	33.0	17.3	16.8							CDCl ₃	[158]
3'-Acetyllythionine	132.5	128.2	62.2	53.0	33.8	73.5	74.8	61.5	172.3	82.9	72.1-(CO:169.0), (Me: 20.5)	14.7	72.4	24.8	25.9	170.5	47.3	68.1	28.8	28.9		CDCl ₃	[156]
3'-Acetylirinderine	135.0	128.4	61.9	54.2	34.0	75.2	80.4	62.4	174.3	81.8	72.5-(CO:110.2), (Me 13.9)	21.1	33.1	16.8	17.2							CDCl ₃	[70]
3'-Acetyltrachelanthamine	44.7	30.4	54.1	54.9	25.6	31.5	67.8	67.9	174.3	81.6	72.2-(CO: (Me: 21.1)	169.7),	13.9	32.8	16.7	17.2						CDCl ₃	[128]
Canescine	133.0	127.5	62.6	53.6	34.4	74.4	75.4	62.3	175.1	84.3	69.5	17.2	33.1	17.2	17.1	171.7	46.9	69.1	29.4	29.2		CDCl ₃ /D ₆ -DMSO	[154]
Canescenine	133.0	127.5	62.6	53.6	34.4	74.4	75.4	62.3	175.1	84.3	71.1	16.0	33.1	17.8	14.2	171.7	46.9	69.1	29.4	29.2		CDCl ₃ /D ₆ -DMSO	[154]
Cryptanthine	133.9	125.8	62.9	53.9	34.7	75.4	75.6	60.7	167.7	127.4	139.3	16.0	20.6	175.4	77.4	71.4	16.7	22.6					[65].
Echihumiline	132.8	127.6	62.0	53.7	34.2	73.7	76.1	62.0	174.3	83.1	69.8	18.5	72.4	26.0	24.9	165.5	115.3	159.0	27.7	20.4		CDCl ₃	[91]
Echimidine isomer	133.3	129	63.2	54.1	34.8	74.2	76	62.9	174.7	83.7	70.0	18.9	73.8	26.5	25.2	167.5	128.9	138.2	14.8	12.3		CDCl ₃	[87].
Echiupinine	133.0	128.1	62.3	53.7	34.3	72.8	75.6	62.2	175.1	82.9	68.7	17.2	32.9	17.1	16.9	167.1	115.6	158.1	27.5	20.3		CDCl ₃	[95]
Echiupinine N-oxide	131.8	128.1	78.2	69.1	34.3	71.4	93.7	60.2	174.9	84.0	69.4	16.9	33.2	17.5	17.2	166.2	114.5	160.3	27.6	20.6		CDCl ₃	[95]
7-Epi-echimiplateine N-oxide	132.4	125.9	79.7	70.2	35.8	71.4	96.7	63.6	176.1	86.9	71.1	19.0	75.6	26.3	27.0							D ₂ O	[164]
2'',3''-Epoxyechiumine	noise	128.5	62.7	53.6	34.4	75.3	75.4	62.5	175.1	82.9	69.4	17.1	33.0	16.9	17.3	noise	77.2	60.0	13.6	19.3		CDCl ₃	[63]
Erythro-3''-chloro-2''-hydroxyechiumine	132.6	127.8	62.4	53.7	34.5	75.4	75.8	62.3	173.6	83.0	69.4	16.9	33.0	17.1	17.3	175.1	77.2	62.8	17.9	23.0		CDCl ₃	[63]

Table 4. Cont.

Alkaloid	C-1	C-2	C-3	C-5	C-6	C-7	C-8	C-9	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'	C-1''	C-2''	C-3''	C-4''	C-5''	C-6''	solvent	References	
Tertiary base and N-oxide alkaloids																								
Floridine	44.2	31.2	54.0	54.0	25.4	29.5	67.6	66.2	173.4	83.4	72.7-(CO: (Me: 21.2)		15.1	73.5	26.2	24.9						CDCl ₃	[128]	
Floridinine	43.3	28.6	53.8	54.0	24.6	30.6	68.4	66.2	174.6	82.5	69.8	18.6	73.9	25.0	26.0								CDCl ₃	[128]
Floridimine	44.3	28.7	54.2	54.3	25.3	30.6	67.6	63.2	174.7	84.1	69.9	18.6	73.8	26.0	24.9								CDCl ₃	[128]
Helindicine	134.2	125.3	62.5	55.5	36.7	70.5	80.5	61.7	175.6	84.5	70.5	17.3	34.2	17.2	17.6								CD ₃ OD	[130]
Heliotridine 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester	134.0	123.5	62.0	55.9	35.0	70.8	79.4	62.2	?	?	45.0	25.2	23.1	24.4	73.9- (8':17.4)								CD ₃ OD	[50].
Heliscabine	81.1	38.4	52.8	52.0	36.0	72.8	69.8	70.0	168.1	127.2	139.7	16.0	20.6										CDCl ₃	[139]
Heliospathine	133.1	128.9	62.4	53.9	36.1	70.5	78.2	62.2	174.5	84.4	71.2	17.4	38.9	24.7	12.1- (8':11.9)								CDCl ₃	[140]
Heliospathuline	139.1	124.2	62.4	53.9	34.8	76.5	76.2	59.3								174.3	83.8	72.4	16.5	31.9	15.6 (7':17.2)		CDCl ₃	[140]
Hydroxymyoscorpine	132.8	128.5	62.8	53.7	34.3	73.8	75.7	62.5	174.2	83.0	69.6	18.4	73.5	25.9	24.8	167.1	128.6	137.8	14.4	11.9			CDCl ₃	[95]
Isoechinatine (9-(+)-viridiflorylheliotridine)	136.1	126.3	61.7	54.3	33.8	74.7	79.8	61.9	174.3	83.9	71.6	17.5	32.2	17.8	15.9								CDCl ₃	[72,75]
Iso-lycopsamine	139.1	123.2	63.0	53.4	34.9	76.4	76.5	59.5								174.1	82.8	69.4	16.5	33.38	17.2 (7':1227)		CDCl ₃	[133]
Lactodine	138.1	123.2	63.8	54.1	35.1	69.4	76.5	58.9	173.3	68.4	16.3												CDCl ₃	[187]
Leptanthine	133.7	124.6	61.7	54.9	36.3	70.0	79.9	61.6	174.8	85.1	70.2	18.0	74.2	26.0	25.4								CD ₃ OD	[166].
Lithosenine N-oxide	133.7	124.0	78.0	69.7	36.3	71.2	96.8	62.5	175.5	86.1	71.2	19.1	75.2	27.0	26.3								CD ₃ OD	[166].
Lithosenine	133.0	126.9	62.2	53.1	33.8	73.4	74.8	61.4	173.5	83.4	68.9	18.0	72.5	24.7	25.9	170.3	47.5	68.1	28.9	29.0			CDCl ₃	[156]
Megalanthonine	36.0	31.2	51.1	54.6	36.8	69.5	72.8	66.2	174.5	84.1	72.0	17.0	32.0	15.6	17.8								CDCl ₃	[134]
Methylechiuplatine	133.5	128.0	62.9	54.0	34.7	73.6	76.1	61.3	171.3	44.9	69.7	44.8	172.2	51.8: OMe	27.3	166.9	127.7	139.2	15.9	20.6			CDCl ₃	[65]

Table 4. Cont.

Alkaloid	C-1	C-2	C-3	C-5	C-6	C-7	C-8	C-9	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'	C-1''	C-2''	C-3''	C-4''	C-5''	C-6''	solvent	References
Tertiary base and N-oxide alkaloids																							
Myoscorpine	133.1	128.1	62.7	53.8	34.4	73.7	75.8	62.2	175.1	82.9	69.3	17.2	32.9	17.1	16.9	167.0	128.5	137.8	14.4	11.9		CDCl ₃	[95]
Myoscorpine N-oxide	131.8	124.0	78.4	69.3	34.3	72.4	93.8	60.1	14.9	84.0	69.4	16.9	33.1	17.5	17.2	166.2	127.9	139.0	14.6	12.0		CDCl ₃	[95]
Onosmectine N-oxide	133.5	123.8	78.6	69.7	35.7	70.7	96.7	62.5	175.3	85.7	74.6	70.8	18.7	26.6	25.9							CD ₃ OD	[164]
(7S, 8R)-Petranine	134.4	121.1	70.9	63.4	34.7	70.2	87.7	59.8	167.5	126.9	140.3	16.1	20.6				68.8					CDCl ₃	[89]
(7S, 8S)-Petranine	134.6	121.3	71.2	63.6	34.8	70.6	88.1	59.9	167.0	127.0	149.9	16.3	20.8				69.1					CDCl ₃	[89]
Platynecine N-oxide																							
2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester	37.3	30.6	73.0	70.6	35.8	70.1	91.5	67.3	?	?	44.5	25.3	23.3	24.8	73.9-(8:17.4)							CD ₃ OD	[50]
Pycnanthine	132.8	126.0	62.2	53.9	34.2	72.4	75.8	61.7	174.4	83.6	71.3	15.8	32.0	17.7	17.0	165.5	112.4	160.1	66.8	30.3		CDCl ₃	[91]
Retronecine 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester	133.2	123.8	62.0	54.0	36.7	70.0	80.0	61.0	175.4	82.3	45.2	25.3	23.3	24.6	73.9-(8:17.6)							CD ₃ OD	[51]
Retronecine N-oxide																							
2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester	133.9	123.4	78.8	70.0	35.7	70.6	97.2	62.4	175.9	82.0	45.0	25.2	23.3	24.6	73.6-(8:17.7)							CD ₃ OD	[51]
Retronecine N-oxide																							
2S-hydroxy-2S-(1R-hydroxyethyl)-4-methyl-pentanoyl ester	134.0	123.4	78.8	70.0	35.8	70.6	97.0	62.0	175.5	81.0	44.0	25.8	23.9	24.3	74.0-(8:16.5)							CD ₃ OD	[51]

Table 4. Cont.

Alkaloid	C-1	C-2	C-3	C-5	C-6	C-7	C-8	C-9	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'	C-1''	C-2''	C-3''	C-4''	C-5''	C-6''	solvent	References	
Tertiary base and N-oxide alkaloids																								
Retronecine 2S-hydroxy-2S-(1S-hydroxyethyl)-2S-[(1'S-hydroxyethyl)-4-methylpentanoyl]-4-methyl-pentanoyl ester	135.4	124.0	62.0	54.9	36.6	70.4	79.8	61.7	175.7	82.2	43.6	25.2	24.0	24.7	73.4-(8':7.4)	180.0	81.3	45.0	25.2	23.1	24.7 (7'':73.6) (8'':17.0)	CD ₃ OD	[51]	
Symviridine	133	127.8	62.7	53.8	34.3	72.7	75.8	62.3	174.4	83.4	70.7	17.1	32.9	17.7	16.0	166.9	115.5	158.2	27.5	20.3		CDCl ₃	[172]	
Supinidine N-oxide 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester	137.7	123.0	76.9	71.1	25.2	28.3	90.2	61.2	176.2	82.0	45.2	25.2	23.5	24.6	73.3-(8':17.6)							CD ₃ OD	[51]	
Tessellatine	138.6	124.5	63.0	53.4	34.7	75.7	76.0	59.6								173.1	83.5	71.4	16.9	31.9	17.6 (7'':15.7)	CDCl ₃	[42]	
Threo-2'',3''-dihydroxyechiumine	132.9	125.0	63.3	54.0	34.8	74.9	75.8	63.0	174.9	83.2	69.8	16.9	33.2	17.2	17.2	175.4	78.7	71.5	16.5	22.1		CDCl ₃	[63]	
Trachelanthamidine 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester	48.0	29.7	55.9	55.8	25.6	31.3	71.9	63.4	181.6	81.8	44.1	25.0	24.0	25.0	73.9-(8':17.4)							CD ₃ OD	[51]	
Uplandicine	132.7	127.7	62.1	53.4	34.0	73.6	75.5	62.2	174.2	83.2	69.6	18.5	73.6	24.7	25.9	170.2	21.1	-	-	-		CDCl ₃	[163]	
Viridiflorine	44.5	31.5	54.5	54.2	25.5	30.0	67.8	67.2	174.4	83.6	71.0	17.2	32.1	17.9	15.9									[42]
Viridinate	139.3	124.2	64.2	54.2	36.7	77.3	77.3	59.4	174.1	82.8	68.4	16.2	33.5	17.2	17.3	176.2	83.2	69.1	16.8	34.12	18.1 (7'':18.9)	CDCl ₃	[187]	
Viridinate N-oxide stereoisomer	132.5	125.4	79.5	70.1	35.8	71.3	96.6	63.3	176.6	85.9	70.9	17.6	34.6	18.9	18.4	176.1	86.2	72.3	18.6	34.2	18, 17.2			

Table 5. ¹H NMR data of new PAs of in the time frame 1995–2013.

Alkaloid	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-9	H-3'	H-4'	H-5'	H-6'	C-7'	H-2''	H-3''	H-4''	H-5''	solvent	References
Necine Base																			
Helibractinecine [C ₈ H ₁₅ NO ₃]		1.94	α 3.13 β 2.93	α 3.07 β 2.91	2.03	4.50	3.34	α 3.60 β 3.66										CDCl ₃ - CD ₃ OD	[111]
Helibracteatinecine [C ₈ H ₁₅ NO ₃]		1.63	α 3.26 β 2.55	α 3.26 β 2.52	α 1.84 β 2.11	3.94	3.12	α 3.79 β 3.84										CDCl ₃ - CD ₃ OD	[112]
Turneforicidine [C ₈ H ₁₅ NO ₂]	2.53	α 1.68 β 2.10	α 3.08 β 2.55	α 3.03 β 2.70	α 2.00 β 1.99	4.18	3.16	α 3.57 β 3.53										CD ₃ OD- ND ₃	[222]
Transalpinecine [C ₈ H ₁₅ NO ₃]		4.18	α 3.86 β 3.38	α 3.06 β 3.36	α 1.95 β 2.16	α 1.88 β 2.66	3.99	α 3.90 β 3.61										CD ₃ OD	[145]
Subulacine [C ₈ H ₁₅ NO ₂]		3.95	α 3.79 β 3.38	α 2.97 3.62	α 1.96 2.24	α 2.19 2.26	4.45	α 3.97 β 3.79										CD ₃ OD	[145]
1α-2α-epoxy-1β- hydroxymethyl-8α- pyrrolizidine [C ₈ H ₁₅ NO ₂]		4.59	α 3.81 β 3.89	α 3.23 β 3.50	α 2.08 β 2.23	α 2.00 β 2.30	4.31	α 3.93 β 3.69										CD ₃ OD	[145]
Tertiary base and N-oxide alkaloids																			
3'-Acetylcanescine [C ₂₂ H ₃₅ NO ₈]		5.83	α 3.95 β 3.38	α 3.33 β 2.65	2.09	5.38	4.35	α 4.79 β 4.67	5.21- (COMe: 2.00)	1.19	2.00	0.94	0.91	2.45		1.26	1.26	CDCl ₃ /D ₆ -DMSO	[154]
3'-Acetylcanescenine [C ₂₂ H ₃₅ NO ₈]		5.83	α 3.95 β 3.38	α 3.33 β 2.65	2.09	5.38	4.35	α 4.74 β 4.73	5.17- (COMe: 2.03)	1.19	2.00	0.94	0.91	2.45		1.26	1.26	CDCl ₃ /D ₆ -DMSO	[154]
3'-Acetylechihumiline N-oxide [C ₂₂ H ₃₃ NO ₉]		6.03	α 4.37 β 4.69	3.90 – 3.75 (m)	α 2.20 β 2.78	5.76	4.83	4.72	5.46- (COMe: 1.98)	1.34		1.25	1.35	5.67	-	1.92	2.18	CD ₃ OD	[166]
3'-Acetylechinatine [C ₁₇ H ₂₇ NO ₆]		5.76	α 3.37 β 3.92	α 2.68 β 3.30	α 1.91 β 1.98	4.17	3.96	α 4.78 β 4.96	5.21- (COMe: 2.04)	1.29	2.01	0.88	0.96					CDCl ₃	[70]
7-Acetylechinatine N- oxide		6.00	α 4.70 β 4.38	α 3.83 β 3.79	α 2.74 β 2.23	5.69	4.88	4.78	3.96	1.42	2.17	0.90	0.93	2.06				CD ₃ OD	[164]

Table 5. Cont.

Alkaloid	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-9	H-3'	H-4'	H-5'	H-6'	C-7'	H-2''	H-3''	H-4''	H-5''	solvent	References
Tertiary base and N-oxide alkaloids																			
7-Acetyლეოპინე [C ₁₈ H ₂₉ NO ₇]		5.81	α 4.02 β 3.38	α 3.28 β 2.86	1.93	5.09	4.16	α 4.93 β 4.87	3.81- (OMe: 3.27)	1.27		1.19	1.31	2.06				CDCl ₃	[110]
3'-Acetyლინდინე [C ₁₇ H ₂₇ NO ₆]		5.92	α 3.96 β 3.45	α 3.29 β 2.76	α 1.98 β 2.02	4.30	4.21	4.80	5.20- (COMe: 2.04)	1.23	2.09	0.95	0.92					CDCl ₃	[158]
3'-Acetyლინდინე N-ოქსიდე [C ₁₇ H ₂₇ NO ₇]		5.79	4.45	3.73- 3.80	α 2.01 β 2.62	4.70	4.66	4.83	5.23- (COMe: 2.03)	1.24	2.05	0.97	0.91					CDCl ₃	[158]
3'-Acetyლლითოსენინე [C ₂₂ H ₃₅ NO ₉]		5.75	α 3.77 β 3.29	α 3.17 β 2.54	1.96	5.23	4.16	α 4.68 β 4.59	5.28- (COMe: 1.87)	1.13		1.25	1.11	2.33		1.17	1.17	CDCl ₃	[156]
3'-Acetyლრინდერინე [C ₁₇ H ₂₇ NO ₆]		5.76	α 3.37 β 3.92	α 2.68 β 3.30	α 1.91 β 1.98	4.21	3.96	α 4.66 β 4.93	5.28- (COMe: 2.02)	1.25	2.01	0.92	0.98					CDCl ₃	[70]
3'-Acetyლტრახელანთამინე [C ₁₇ H ₂₉ NO ₅]	2.09	α 1.70 β 2.02	α 3.28 β 2.60	α 3.07 β 2.65	α 1.89 β 1.84	α 2.05 β 1.63	3.38	4.16	5.22- (COMe: 1.97)	1.23	2.02	0.90	0.96					CDCl ₃	[128]
Canescine [C ₂₀ H ₃₃ NO ₇]		5.83	α 3.95 β 3.38	α 3.33 β 2.65	2.09	5.38	4.35	α 4.79 β 4.67	4.07	1.19	2.00	0.94	0.91	2.45		1.26	1.26	CDCl ₃ / D ₆ -DMSO	[154]
Canescenine [C ₂₀ H ₃₃ NO ₇]		5.83	α 3.95 β 3.38	α 3.33 β 2.65	2.09	5.38	4.35	α 4.74 β 4.73	3.89	1.19	2.00	0.94	0.91	2.45		1.26	1.26	CDCl ₃ / D ₆ -DMSO	[154]
Cryptanthine		5.74	α 4.0 β 3.37	α 3.40 β 2.61	2.12	5.3	4.39	α 4.84 β 4.64	-	6.1	1.98	1.89		3.8	1.17	1.24		CDCl ₃	[65]
5'-Deoxyლასიოკარპინე [C ₂₁ H ₃₃ NO ₆]		5.8	α 3.50 β 4.18	α 3.00 β 3.40	1.8	5.12	4.37	4.88	3.7- (OMe: 3.22)	1.21	2.20	0.95	0.94		6.13	1.95	1.82	CDCl ₃	[123]
Echihumiline [C ₂₀ H ₃₁ NO ₇]		5.87	α 3.35 β 3.72	α 2.83 β 2.83	2.09	5.48	4.13	α 4.65 β 4.96	4.21	1.26	-	1.24	1.31	5.59	-	1.90	2.15	CDCl ₃	[91]
Echihumiline N-ოქსიდე [C ₂₀ H ₃₁ NO ₈]		5.97	α 4.54 β 4.77	α 3.73 β 4.13	α 2.24 β 2.89	5.77	5.45	α 4.71 β 4.94	4.22	1.27	-	1.25	1.30	5.57	-	1.92	2.17	CDCl ₃	[91]
Echimidine isomer (tigloyl) [C ₂₀ H ₃₁ NO ₇]		5.81	α 3.34 β 3.83	α 2.60 β 3.27	2.05	5.37	4.32	α 4.60 β 4.86	4.12	1.21		1.17	1.26	-	6.05	1.91	1.76	CDCl ₃	[87].

Table 5. Cont.

Alkaloid	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-9	H-3'	H-4'	H-5'	H-6'	C-7'	H-2''	H-3''	H-4''	H-5''	solvent	References
Tertiary base and N-oxide alkaloids																			
7-Epi-echimiplatine N-oxide [C ₁₅ H ₂₅ NO ₇]		5.89	α 4.42 β 4.21	α 3.74 β 3.59	α 2.47 β 2.01	4.67	4.55	4.78	4.18	1.14		1.16	1.21					D ₂ O	[164]
Floridine [C ₁₇ H ₂₉ NO ₆]	2.23	α 2.15 β 2.15	α 3.75 β 2.77	α 3.48 β 2.65	2.04	α 2.20 β 1.70	4.01	α 4.16 β 4.27	5.45 - (COMe: 1.98)	1.36	-	1.25	1.40					CDCl ₃	[128]
Floridinine [C ₁₅ H ₂₇ NO ₅]	2.36	α 2.08 β 2.20	α 3.51 β 2.66	α 3.24 β 2.85	α 2.0 β 1.94	α 2.15 β 1.63	3.70	α 4.20 β 4.53	4.19	1.27	-	1.28	0.96					CDCl ₃	[128]
Floridimine [C ₁₅ H ₂₇ NO ₅]	2.30	α 2.17 β 2.28	α 3.89 β 2.83	α 3.59 β 2.89	2.11	α 2.26 β 1.80	4.30	α 4.35 β 4.45	4.26	1.32	-	1.28	1.33					CDCl ₃	[128]
Helibracteatine [C ₁₃ H ₂₁ NO ₄]		1.85	α 3.22 β 2.54	α 3.22 β 2.54	α 1.85 β 2.05	4.08	3.30	α 4.35 β 4.46	6.10	1.99	1.91							CDCl ₃ + D ₂ O	[112]
Helibracteatinine [C ₁₃ H ₂₁ NO ₄]		α 1.80 β 2.10	α 3.35 β 2.78	α 3.20 β 2.60	1.80	5.09	3.30	α 3.64 β 3.84							6.12	1.98	1.88	CDCl ₃ + D ₂ O	[112]
Helindicine [C ₁₅ H ₂₃ NO ₄]		5.94	α 4.40 β 3.92	α 3.97 β 3.34	2.15	4.63	4.90	α 4.98 β 4.80	4.05	1.17	2.03	0.95	0.93					CD ₃ OD	[130]
Heliotridine 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester [C ₁₆ H ₂₇ NO ₅]		5.95	3.70 4.18	3.10 2.64	2.10	4.52	4.60	4.85	1.74 1.79	1.82	0.87	0.99	3.78- (8':1.15)					CD ₃ OD	[50]
Heliscabine [C ₁₃ H ₂₁ NO ₄]		1.86	α 3.42 β 3.05	α 3.30 β 3.05	2.16	4.66	3.64	α 4.25 β 4.35	6.10	1.99	1.89							CDCl ₃	[139]
Ilamine [C ₁₆ H ₂₇ NO ₅]		5.81	3.45 4.10	2.62 3.35	1.86	1.66 2.10	4.43	4.78	3.81	1.28		1.31	1.20 (8-OMe: 3.30)					CDCl ₃	[115]
Ilamine N-oxide [C ₁₆ H ₂₇ NO ₆]		5.81	α 3.43 β 4.55	α 3.48 β 3.79	α 1.99 β 1.89	2.50	4.81	α 4.85 β 4.69	3.80	1.26		1.29	1.22- (8-OMe:3.30)					CDCl ₃	[115]

Table 5. Cont.

Alkaloid	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-9	H-3'	H-4'	H-5'	H-6'	C-7'	H-2''	H-3''	H-4''	H-5''	solvent	References
Tertiary base and N-oxide alkaloids																			
<i>Isoechinatine</i> (9-(+)- Viridiflorylheliotridine) [C ₁₅ H ₂₅ NO ₅]		5.66	3.30 3.83	2.55 3.22	1.80 1.92	4.13	3.97	4.70 5.00	3.92	1.24	2.13	0.89	0.85					CDCl ₃	[72,75]
Leptanthine [C ₁₅ H ₂₅ NO ₆]		5.90	α 3.90 β 4.40	3.90	2.20	4.65	4.95	4.90	4.20 – Me 1.98	1.29	1.28	1.32							[166]
Leptanthine N-oxide [C ₁₅ H ₂₅ NO ₇]		6.05	α 4.65 β 4.85	4.1–4.0 (m)	α 2.23 β 2.63	4.83	5.20	α 4.92 β 4.98	4.22 – Me 1.98	1.28	1.25	1.31							[166]
Lactodine [C ₁₁ H ₁₇ NO ₄]		5.68	α 3.90 β 3.34	α 3.26 β 2.59	α 1.93 β 1.87	4.10	4.02	α 5.01 β 4.89	4.20	1.39								CDCl ₃ + D ₂ O	[187]
Lithosene [C ₂₀ H ₃₃ NO ₈]		5.78	α 3.77 β 3.29	α 3.16 β 2.57	1.96	5.21	4.20	α 4.66 β 4.52	4.03	1.13		1.17	1.11	2.33		1.16	1.16	CDCl ₃	[156]
Megalanthonine [C ₁₅ H ₂₇ NO ₅]	2.78	α 1.89 β 2.15	α 3.26 β 2.61	α 3.21 β 2.73	α 2.03 β 2.14	4.29	3.48	α 4.09 β 4.46	2.64	-	2.64	3.70	1.34		6.80	1.96	1.80	CDCl ₃	[134]
Methylechiuplatine [C ₂₀ H ₂₉ NO ₇]		5.77	α 3.97 β 3.37	α 3.32 β 2.64	2.09	5.40	4.33	α 4.68 β 4.62											[65].
Neo coramandaline [C ₁₅ H ₂₇ NO ₄]	1.9	α 1.85 β 1.55	α 3.20 β 2.50	α 3.05 β 2.64	α 1.85 β 1.55	α 1.90 β 1.35	3.56	α 4.30 β 4.20	3.98	1.23	2.14	0.88	0.92					CDCl ₃	[74]
Onosmerectine N-oxide [C ₁₅ H ₂₅ NO ₇]		5.96	α 4.66 β 4.45	3.87	α 2.58 β 2.12	4.75	4.85	α 4.92 β 4.88		4.22	1.26	1.31	1.27					CD ₃ O	[164]
(7S, 8R)-Petranine [C ₁₄ H ₂₀ CINO ₃]		5.82	α 4.55 β 4.77	α 4.09 β 4.35	α 2.48 β 2.70	4.92	5.36	4.78	6.18	2.00	1.90			α 5.42 β 5.75				CDCl ₃	[89]
(7S, 8S)-Petranine [C ₁₄ H ₂₀ CINO ₃]		5.83	α 4.54 β 4.78	α 4.09 β 4.35	α 2.51 β 2.69	4.94	5.38	4.88	6.20	2.02	1.90			α 5.71 β 5.39				CDCl ₃	[89]

Table 5. Cont.

Alkaloid	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-9	H-3'	H-4'	H-5'	H-6'	C-7'	H-2''	H-3''	H-4''	H-5''	solvent	References
Tertiary base and N-oxide alkaloids																			
Platynecine N-oxide 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester [C ₁₆ H ₂₉ NO ₆]	2.22	α 1.90 β 2.33	α 3.30 β 3.89	α 3.61 β 3.87	α 2.07 β 2.14	4.52	3.84	α 4.29 β 3.85	α 1.76 β 1.70	1.82	0.87	0.98	3.78- (8':1.15)					CD ₃ OD	[50]
Pycnanthine [C ₂₀ H ₃₁ NO ₇]		5.83	α 3.55 β 4.06	α 2.80 β 3.50	2.15	5.47	4.12	α 4.65 β 4.75	3.99	1.26	2.15	0.93	0.85	5.92	-	3.65	2.06	CDCl ₃	[91]
Retronecine 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester [C ₁₆ H ₂₇ NO ₅]		5.96	α 3.98 β 4.46	α 3.49 β 3.87	2.19	4.64	4.90	4.95	1.75	1.83	0.88	0.99	3.78 8':1.17					CD ₃ OD	[51]
Retronecine N-oxide 2S-hydroxy-2S-(1S-hydroxyethyl)-4-methyl-pentanoyl ester [C ₁₆ H ₂₇ NO ₆]		5.93	α 4.36 β 4.65	α 3.70 β 3.82	α 2.63 β 2.08	4.72	4.68	4.85	α 1.73 β 1.80	1.82	0.88	0.98	3.76- (8':1.16)					CD ₃ OD	[51]
Retronecine N-oxide 2S-hydroxy-2S-(1R-hydroxyethyl)-4-methyl-pentanoyl ester [C ₁₆ H ₂₇ NO ₆]		5.95	α 4.36 β 4.60	α 3.70 β 3.85	α 2.60 β 2.08	4.72	4.69	4.82	α 1.66 β 1.47	1.74	0.88	1.00	3.91- (8':1.22)					CD ₃ OD	[51]
Retronecine 2S-hydroxy-2S-(1S-hydroxyethyl)-2S-[(1'S-hydroxyethyl)-4-methylpentanoyl]-4-methyl-pentanoyl ester [C ₂₄ H ₄₁ NO ₈]		5.95	α 3.96 β 4.39	α 3.29 β 3.89	2.18	4.61	4.91	4.94	α 1.79 β 1.82	1.80	0.95	0.99	3.70- (8':1.16)	1.79	1.85	α 1.81 β 0.87	3.77- (6'':1.14)	CD ₃ OD	[51]

Table 5. Cont.

Alkaloid	H-1	H-2	H-3	H-5	H-6	H-7	H-8	H-9	H-3'	H-4'	H-5'	H-6'	C-7'	H-2''	H-3''	H-4''	H-5''	solvent	References
Tertiary base and N-oxide alkaloids																			
Symviridine [C ₂₀ H ₃₁ NO ₆]		5.84	α 4.02 β 3.43	α 3.40 β 2.68	2.10	5.41	4.48	α 4.78 β 4.66	3.97	1.22	2.13	0.86	0.92	5.57	-	1.88	2.12	CDCl ₃	[172]
Supinidine N-oxide 2S- hydroxy-2S-(1S- hydroxyethyl)-4-methyl- pentanoyl ester [C ₁₆ H ₂₇ NO ₄]		5.90	α 4.36 β 4.56	α 3.61 β 3.67	α 2.08 β 2.38	2.50 2.03	4.66	4.77	α 1.73 β 1.80	1.83	0.88	0.98						CD ₃ OD	[51]
Trachelanthamidine 2S- hydroxy-2S-(1S- hydroxyethyl)-4-methyl- pentanoyl ester [C ₁₆ H ₂₉ NO ₄]	2.28	1.90 2.27	α 3.22 β 3.48	α 3.74 β 3.12	2.08 2.19	2.25 1.97	3.99	3.69 3.63	1.77 1.69	1.83	0.94	1.00	3.77- (8':1.15)					CD ₃ OD	[51]
Uplandicine [C ₁₇ H ₂₇ NO ₇]		5.83	α 3.38 β 3.93	α 2.70 β 3.35	2.06	5.34	4.43	α 4.62 β 4.87	4.14	1.22	-	1.26	1.19	1.98				CDCl ₃	[163]
Viridinate [C ₂₂ H ₃₇ NO ₈]		5.71	α 3.80 β 3.30	α 3.16 β 2.19	α 1.92 β 1.85	5.48	4.10	α 4.98 β 4.76	3.90	1.28	2.15	0.86	0.93	-	3.95	1.32	2.14 (6':0.90) (7':1.00)	CDCl ₃ + D ₂ O	[187]
Viridinate N-oxide stereoisomer [C ₂₂ H ₃₇ NO ₉]		5.86	α 4.51 β 4.22	α 3.73 β 3.61	α 2.45 β 2.00	4.67	5.57	4.75	4.04	1.04	1.89	0.75–0.78		-	3.93	1.10	2.05, 0.81	D ₂ O	[164]

5. Biological Activity of PAs

5.1. Antimicrobial Activity

The growth of bacterial species, mostly human pathogens such as *E. coli*, *S. pneumoniae*, *Bacillus subtilis*, *B. anthracis* and *Staphylococcus aureus* were inhibited by different pure PAs and PA extracts [90,110]. Successive root bark extracts of *Cordia gillettii* (Boraginaceae) were tested for their antimicrobial activity against 10 strains of bacteria and 1 strain of fungi by broth microdilution and agar diffusion methods. The methanol extract showed direct antimicrobial activity against all tested microorganisms with minimum inhibitory concentrations (MIC) ranging between 125 and 1,000 µg/ml. [223]. Joosten and van Veen [224] discussed the impact of plant-produced PAs on plant-associated microorganisms, their detoxification by microorganisms and the ecological consequences of this activity.

5.2. Sequestration in Insects and Antifeedant Properties

Several insects are PA specialists which not only tolerate PAs of their host plants but use them for their own chemical defence against predators, as morphogens and even as pheromones [101,144,225–231]. Defensive PAs can be obtained as larvae from food plants and as adults via nectar. PA sequestering insects often show aposematic colouration. Several moths and butterflies use unsaturated PAs to produce dihydropyrrrolizidines with pheromone activity [110]. In some moths PAs are morphogens inducing the formation of large coremata in males, which function as pheromone emitting organs. A recent review published by Macel [232], threw light on the dual role PAs in plant-insect interactions.

The antifeedant activity of six PAs isolated from *Anchusa strigosa* towards the generalist herbivore *Spodoptera exigua* and the cabbage specialist *Pieris brassicae* was evaluated [50]. 1,2-Unsaturated PAs (e.g., retronecine 2S-hydroxy (1S-hydroxyethyl)-4-methyl-pentanoyl ester and its N-oxide) reduced feeding by *P. brassicae* by 52 and 68%, respectively compared to control. However, the alkaloids lacking to 1,2-double bond (trachelanthamidine ester and platynecine ester) showed no deterrent activity.

5.3. Biological Importance

Toxicity of 1,2-unsaturated PAs as hepatotoxic, pulmotoxic, hemolytic, antimitotic, teratogenic, mutagenic and carcinogenic natural products for humans and livestock is well documented [23–32,35,36]. The potential PA contamination of food and feeding stuff has attracted recurrent attention. It is evident, that humans should not ingest food or herbal teas that contain PAs. However, some saturated PAs have interesting pharmacological and biological effects, e.g., spasmolytic, antihistaminic, anti-HIV and antiviral activities and as glucosidase inhibitor [233–235]. *Solanecio angulatus* and *Crotalaria phillipsiae* (PA containing plants from the families Asteraceae and Fabaceae) serve as sources of novel trypanocidal compounds [236]. The crude ethanol and hexane extracts of *Heliotropium subulatum* showed significant antiviral activity to Cocksackie, Poliomyelitis and Measles at 500 and 100 µg/mL, respectively, while heliotrine and 7-angeloylheliotrine demonstrated activity against Poliomyelitis and Vesicular stomatitis at concentration of 10 µg /mL [237]. PAs can inhibit the specific binding of

radioligands to muscarinic acetylcholine and serotonin receptors and to a lesser degree to adrenergic receptors [20]. This neuromodulatory effect might be responsible for the avoidance of PA plants by many herbivores.

6. Chemotaxonomic Information of PAs in Boraginaceae

The distribution of PAs is documented in Tables 1 and 2. A comparison of phytochemical occurrences of alkaloids with regard to recent results in the molecular phylogeny of the Boraginaceae was not intended in this review, but will be part of a separate publication. It has been shown previously that the occurrence of PAs in the plant kingdom does not necessarily mirror phylogenetic relatedness because the genes which encode the enzymes of alkaloid biosynthesis can be switched on or off [2,238].

6.1. Genus *Amsinckia*

PA profiles of twenty species and varieties of the genus *Amsinckia* have been investigated. All identified alkaloids were from retronecine, (+)- and (–)-supinidine, (+)-isoretrenocanol and trachelanthamidine types [42–44,46,104].

6.2. Genus *Cynoglossum*

Plants belongs to this genus contain alkaloids mainly derived from heliotridine type, in addition to (+)- and (–)-supinidine and trachelanthamidine bases [60,67–78,80–86,239].

6.3. Genus *Echium*

PAs of about 15 species from this genus have been investigated which accumulate PAs from retronecine type [11,28,29,60,87,89–93,96,99]. However, in earlier papers [47,97,98], the structure of major compounds in *Echium vulgare* were wrongly assigned to heliosupine and 3'-acetylheliosupine by means of paper chromatography and/or mass spectrometry. These compounds belong to heliotridine types. Recent publications revised the structures to the stereoisomeric analogue, echimidine and 3'-acetylechimidine (retronecine type), based on NMR and other advanced spectroscopic techniques [11,96,229].

6.4. Genus *Heliotropium*

Biosynthetic studies on necines that have been incorporated into PAs as well as the isolated and/or identified alkaloids in the genus *Heliotropium* indicated that it contains retronecine, (–)-trachelanthamidine, (–)-supindine, (–)-isoretrenocanol, laburnine, lindelofidine, platynecine and subulacine nucleus, in addition heliotridine type PAs [28,29]. In addition to the isolation of the open-chained necines, a cyclic diester PA, e.g., helindicine has been recorded in *H. indicum* [130], incanine in *H. olgae* and trichodesmine in *H. arguzioides* [29].

6.5. Genus *Paracaryum* and *Paracynoglossum*

Only PAs from the heliotridine and (–)-trachelanthamidine type have been reported to be accumulated in these species [28,29,40,151].

6.6. Genus *Rindera*

All the previously examined *Rindera* species contain heliotridine-type PAs [120,152,169]. Echinatine is considered as a chemotaxonomical marker in this genus.

6.7. Genus *Symphytum*

Eleven *Symphytum* species (*S. aintabicum*, *S. bohemium*, *S. consolidum*, *S. grandiflorum*, *S. ibericum*, *S. orientale*, *S. peregrinum*, *S. sylvaticum* subsp. *sepulcrale* var. *sepulcrale*, *S. tanaiense*, *S. tuberosum*, *S. × uplandicum*) have been documented to synthesis pyrrolizidine alkaloids of retronecine type [17,29,170,177]. However, both retronecine and heliotridine type alkaloids were identified in *S. asperum* [171], *S. caucasium* [174], and *S. officinale* [29].

6.8. Other Boraginaceae Species

Species of genus *Alkanna* [40,41,184], *Cryptantha* [63–66], *Mertensia* [157], and *Messerschmidia* [158] produce only PAs of the retronecine type. Whereas *Onosma heterophyllum* and *O. erecta* [164] accumulate only heliotridine type PAs, other species of this genus synthesise retronecine type PAs [60,161,163,166,167] in addition to, supinidine [163] and trachelanthamidine type [167].

7. Conclusions

Our knowledge on PAs in Boraginaceae has improved substantially during the last decades, especially as advanced analytical methods, such as GLC, HPLC in combination with mass spectrometry have been widely applied. However, information on the biochemistry and physiology of PAs in plants and their function in plant insect interactions is still limited. More research has addressed pharmacological and toxicological properties of PAs in food plants and herbal medicines; public awareness is rightly concerned with PAs in food items and their place in the food chain. This review summarizes the state of our existing knowledge.

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Author Contributions

This review was planned by both authors. Assem El-Shazly collected the information and drafted the manuscript which was interpreted and edited by Michael Wink. Both authors finally approved the published version.

Conflicts of Interest

Michael Wink is Editor-in-Chief of Diversity.

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