

Review

Exploring the Biomedical Potential of Terpenoid Alkaloids: Sources, Structures, and Activities

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Abstract: Terpenoid alkaloids are recognized as a class of compounds with limited numbers but potent biological activities, primarily derived from plants, with a minor proportion originating from animals and microorganisms. These alkaloids are synthesized from the same prenyl unit that forms the terpene skeleton, with the nitrogen atom introduced through β -aminoethanol, ethylamine, or methylamine, leading to a range of complex and diverse structures. Based on their skeleton type, they can be categorized into monoterpenes, sesquiterpenes, diterpenes, and triterpene alkaloids. To date, 289 natural terpenoid alkaloids, excluding triterpene alkaloids, have been identified in studies published between 2019 and 2024. These compounds demonstrate a spectrum of biological activities, including anti-inflammatory, antitumor, antibacterial, analgesic, and cardioprotective effects, making them promising candidates for further development. This review provides an overview of the sources, chemical structures, and biological activities of natural terpenoid alkaloids, serving as a reference for future research and applications in this area.

Keywords: terpenoid alkaloids; natural products; biological activity



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1. Introduction

Alkaloids, a diverse class of secondary metabolites, are widely distributed in nature, with more than 27,000 species identified to date, predominantly originating from the plant kingdom, though relatively few are found in the animal and microbial kingdoms [1]. They typically exhibit strong biological activities, including antitumor, antibacterial, insecticidal, and analgesic effects [2–4]. Among the numerous classes of alkaloids, terpenoid alkaloids (TeAs) occupy a pivotal position. These alkaloids are formed from terpenoids through amination reactions, making them aminated terpenes [5]. TeAs are classified as pseudo alkaloids primarily because their biosynthetic origins do not involve the amino acid pathway. Instead, terpenoid moieties in TeAs are biosynthesized from isoprene through the methylerythritol phosphate (MEP) pathway, while nitrogen atoms are typically introduced into the structures of terpenoids in the form of β -aminoethanol, ethylamine, or methylamine [1].

Despite the vast variety of alkaloids and terpenoids isolated from nature, only a tiny proportion of them conform to the structural features of TeAs. TeAs, as a natural product with diverse structures, are primarily divided into monoterpene, sesquiterpene, diterpene, and triterpene alkaloids according to the differences in their skeletons [6]. Among them, monoterpene alkaloids are derived from iridoid compounds, mainly concentrated in the plants of Bignoniaceae, Lamiaceae, Gentianaceae, and Scrophularia [7]. Sesquiterpene alkaloids are the least abundant class of TeAs, which are narrowly distributed in the plant kingdom and mainly concentrated in plants such as *Dendrobium* [5]. Diterpenoid alkaloids

(DAs) are the most complex and numerous compounds in TeAs, mainly concentrated in the *Aconitum* and *Delphinium* plants of Ranunculaceae [8]. In addition, marine sponges are also an important source of diterpenoid alkaloids.

Although small in number, these alkaloids are widely bioactive. For example, incarvilleine, a monoterpene alkaloid with strong analgesic activity, isolated from the traditional Chinese medicine *Incarville sinensis* LAM., has become a significant lead compound in the development of new non-narcotic pain medications [9]. DAs have been used for many years as traditional medicines in China, Japan, Russia, Mongolia, and India [10]. Because of their severe toxicity, in ancient times, *Aconitum* roots were often used to hydrolyze highly toxic DAs (e.g., aconitine) into less toxic derivatives (e.g., benzyllaconine) by soaking, boiling, or other processing methods [8,11]. Modern pharmacological studies have shown that diterpene alkaloids have significant anti-inflammation, analgesia, anticancer, and anti-arrhythmia effects [8]. Moreover, as a diterpenoid alkaloid, Crassicauline A has been clinically utilized as an anti-arrhythmic drug [12]. Similarly, cyclovirobuxine-D, a triterpene alkaloid, is also used clinically as an antiarrhythmic drug [13] and has been recognized as a lead compound for innovative analgesics [14].

The research significance and medical value of TeAs as a class of natural products with unique structures and a wide range of biological activities are clear. Given the complexity and variability of triterpenoid alkaloids' structures and the constraints of space, this paper will focus on the sources, chemical structures, and biological activities of natural TeAs, excluding triterpene alkaloids, discovered in the past five years, hoping to provide a reference for the further research and application of TeAs.

2. Classes of Terpenoidal Alkaloids

2.1. Monoterpenoid Alkaloids

Monoterpenoid alkaloids represent a distinct class of alkaloids derived from iridoid glycosides, typically originating from loganin and secologanin after amination. According to Wang's classification of monoterpene alkaloids, they can be divided into two categories: iridoids and secoiridoids [15]. This section discusses 26 monoterpenoid alkaloids isolated from plants, including 24 iridoid-type alkaloids (1–24) and two secoiridoid-type alkaloids (25–26). Specific plant sources are listed in Table 1. The chemical structure details are shown in Figure 1.

2.1.1. Iridoid-Type Alkaloids (1–24)

The biosynthetic precursors of these alkaloids are iridoid glycosides. Based on the level of hydrogenation within their nitrogen-containing six-membered rings, they can be classified into four subtypes: pyridine ring type, piperidine ring type, dihydropyridine ring type, and tetrahydropyridine ring type [15].

Alstochonines A (1) and B (2) were isolated from the branches of *Alstonia scholaris* (Apocynaceae). Alstochonine A (1) was the first reported C-4 methylated nor-monoterpenoid alkaloid. Alstochonine B (2), processing a cyclopentyl[c]pyridine skeleton, is believed to be biosynthesized from iridotrial by ammonification, aromatization, and oxidation reactions [16].

(R)-10-hydroxyl-4-noractinidine (3) was extracted and isolated from *Rauvolfia vomitoria*'s trunk, the first reported monoterpene alkaloid in *R. vomitoria* (Apocynaceae) [17].

Delavatines C-E (9–11), three monoterpene alkaloids with a cyclopentane[c]piperidine skeleton, were isolated from whole plants of *Incarvillea delavayi* (Bignoniaceae) [18].

Incarvine G (12), a novel monoterpene alkaloid isolated from *Incarvillea sinensis* Lam., is an ester composed of a monoterpene alkaloid with a cyclopentane[c]piperidine skeleton and glucose [19].

Isoxerine (13), isolated from the roots of *Scrophularia ningpoensis*, was named due to its absolute configuration of C-7 being 7S, differing from oxerine [20].

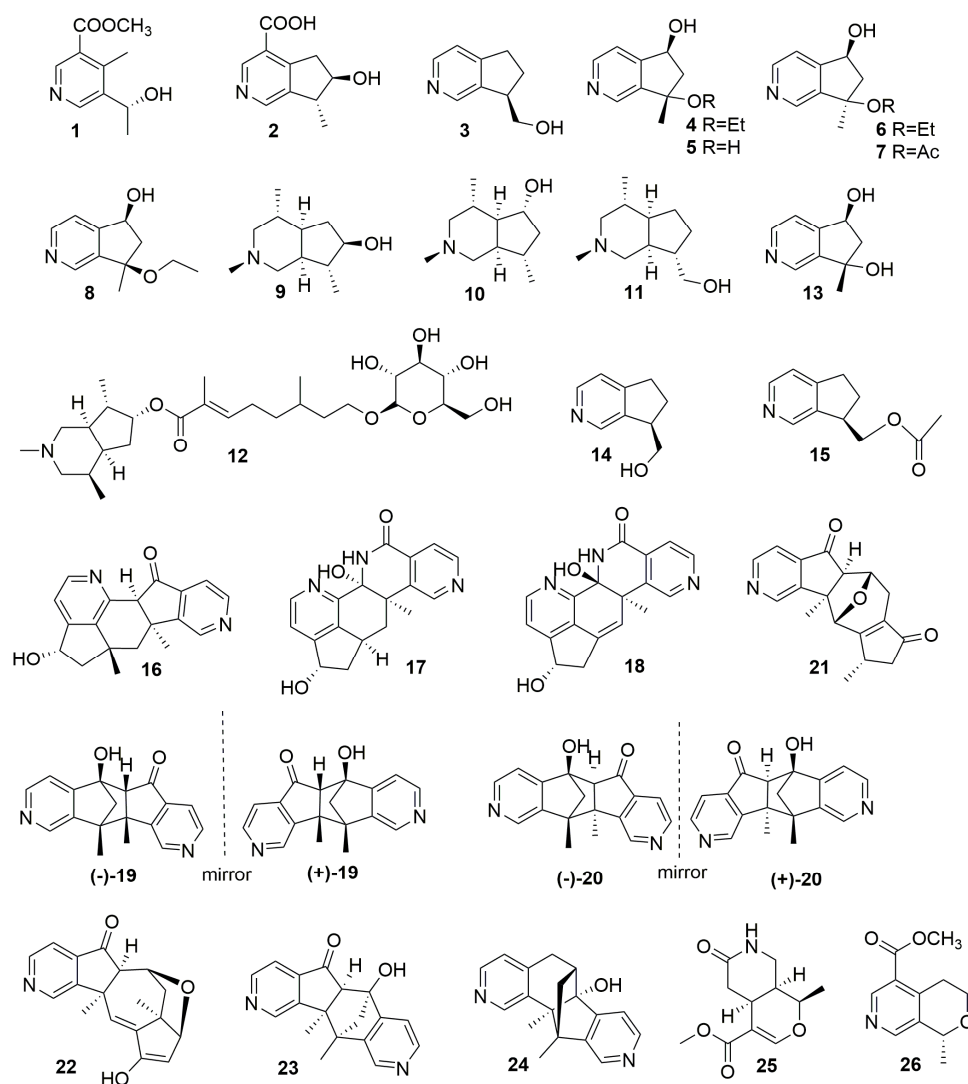


Figure 1. Structures of monoterpene alkaloids (1–26).

Forsyqinlingines C (**14**) and D (**15**) were isolated from the ripe fruits of *Forsythia suspensa* (Oleaceae), with the structures determined by analysis of spectra including HR-ESI and NMR. Both alkaloids belong to a rare class of planar C₉-monoterpenoid alkaloids [21].

The dimeric monoterpene alkaloids (±)-Caryopterisines A (**19**) and B (**20**) were identified as racemates isolated from *Caryopteris glutinosa* Rehder (Lamiaceae), and their absolute configurations were determined using calculated ECD spectra and X-ray diffraction analysis. They are two novel dimers with a 6/5/5/5/6 pentacyclic system. In addition, they can be biosynthesized by oxerine dehydration or oxygenation and subsequent Diels–Alder reactions [22].

Caryopterisines F–I (**4**–**7**) and caryopterisines C–E (**16**–**18**) were subsequently isolated from *C. glutinosa* Rehder. Caryopterisines F–I (**4**–**7**) are four monoterpene alkaloids containing the cyclopentyl[c]pyridine skeleton, while caryopterisines C–E (**16**–**18**) represent three novel dimeric monoterpene alkaloids and are believed to be biosynthesized via the Diels–Alder reaction followed by aromatization rearrangement and a series of subsequent reactions [23]. Of these, caryopterisine C (**16**) has an unprecedented 6/5/6/6/5 pentacyclic ring framework, while caryopterisines D (**17**) and E (**18**) both have 6/6/6/5 fused ring frameworks.

Compounds **8** and **21**–**24** were isolated from the aerial parts of *Caryopteris mongolica* Bunge (Lamiaceae), a medicinal plant in Mongolia. Among them, (5*S**,7*R**)-7-Ethoxy-6,7-dihydro-7-methyl-5*H*-cyclopenta[c]pyridin-5-ol (**8**) is a monoterpene alkaloid

with a cyclopenta[c]pyridine framework [24]. (5aR*,6S*,10S*,11R*,11aR*)-10,11a-Dimethyl-6,7,9,10,11,11a-hexahydro-5H-6,11-epoxycyclopenta [6,7]azuleno [1,2-c]pyridin-5,8(5aH)-dione(**21**) and (5aR*,6S*,7aR*,8S*,11aR*)-10-Hydroxy-7a,11a-dimethyl-5a,6,7,7a,8,11a-hexahydro-5H-6,8-epoxycyclopenta [6,7]azuleno [1,2-c] pyridin-5-one(**22**) could be formed by fusion of the cyclopenta[c]pyridine and 4-Demethyliridoid, and (5R*,5aR*,10bS*,11R*)-5-Hydroxy-10b,11-dimethyl-5,5a,10b,11-tetrahydro-6H-5,11-methanopyrido [3',4':3,4]cyclopenta [1,2-g]isoquinolin-6-one(**23**) and (6S*,6aR*,11R*,11aS*)-6a-Hydroxy-11,11a-dimethyl-6,6a,11,11a-tetrahydro-5H-6,11-methanopyrido [3',4':4,5]cyclopenta [1,2-h]isoquinolin-5-one(**24**) are dimerization products of two cyclopenta[c]pyridine [24].

Table 1. Names and plant sources of monoterpene alkaloids (1–26).

No.	Compound Names	Sources	Plant Parts	Ref.
1	Alstochonine A	<i>Alstonia scholaris</i>	branch	[16]
2	Alstochonine B	<i>Alstonia scholaris</i>	branch	[16]
3	(R)-10-hydroxyl-4-noractinidine	<i>Rauvolfia vomitoria</i>	trunk	[17]
4	Caryopterisine F	<i>Caryopteris glutinosa</i>	whole plant	[23]
5	Caryopterisine G	<i>Caryopteris glutinosa</i>	whole plant	[23]
6	Caryopterisine H	<i>Caryopteris glutinosa</i>	whole plant	[23]
7	Caryopterisine I	<i>Caryopteris glutinosa</i>	whole plant	[23]
8	(5S*,7R*)-7-Ethoxy-6,7-dihydro-7-methyl-5H-cyclopenta[c]pyridin-5-ol.	<i>Caryopteris mongolica</i> Bunge	aerial part	[24]
9	Delavatine C	<i>Incarvillea delavayi</i>	whole plant	[18]
10	Delavatine D	<i>Incarvillea delavayi</i>	whole plant	[18]
11	Delavatine E	<i>Incarvillea delavayi</i>	whole plant	[18]
12	Incarvine G	<i>Incarvillea sinensis</i>	whole herb	[19]
13	Isoxerine	<i>Scrophularia ningpoensis</i>	root	[20]
14	Forsyqinlingine C	<i>Forsythia suspensa</i>	fruit	[21]
15	Forsyqinlingine D	<i>Forsythia suspensa</i>	fruit	[21]
16	Caryopterisine C	<i>Caryopteris glutinosa</i>	whole plant	[23]
17	Caryopterisine D	<i>Caryopteris glutinosa</i>	whole plant	[23]
18	Caryopterisine E	<i>Caryopteris glutinosa</i>	whole plant	[23]
19	(±)-Caryopterisine A	<i>Caryopteris glutinosa</i>	whole plant	[22]
20	(±)-Caryopterisine B	<i>Caryopteris glutinosa</i>	whole plant	[22]
21	(5aR*,6S*,10S*,11R*,11aR*)-10,11a-Dimethyl-6,7,9,10,11,11a-hexahydro-5H-6,11-epoxycyclopenta [6,7]azuleno [1,2-c]pyridin-5,8(5aH)-dione.	<i>Caryopteris mongolica</i> Bunge	aerial part	[24]
22	(5aR*,6S*,7aR*,8S*,11aR*)-10-Hydroxy-7a,11a-dimethyl-5a,6,7,7a,8,11a-hexahydro-5H-6,8-epoxycyclopenta [6,7]azuleno [1,2-c]pyridin-5-one.	<i>Caryopteris mongolica</i> Bunge	aerial part	[24]
23	(5R*,5aR*,10bS*,11R*)-5-Hydroxy-10b,11-dimethyl-5,5a,10b,11-tetrahydro-6H-5,11-methanopyrido [3',4':3,4]cyclopenta [1,2-g]isoquinolin-6-one.	<i>Caryopteris mongolica</i> Bunge	aerial part	[24]
24	(6S*,6aR*,11R*,11aS*)-6a-Hydroxy-11,11a-dimethyl-6,6a,11,11a-tetrahydro-5H-6,11-methanopyrido [3',4':4,5]cyclopenta [1,2-h]isoquinolin-5-one	<i>Caryopteris mongolica</i> Bunge	aerial part	[24]
25	Longiflorine	<i>Uncaria longiflora</i> var. <i>pteropoda</i>	leaf	[25]
26	Lomatogonin C	<i>Lomatogonium carinthiacum</i>	whole plant	[26]

2.1.2. Secoiridoid-Type Alkaloids (25–26)

This kind of alkaloid is mainly distributed in Gentianaceae plants and derived from secoiridoid glycosides [15]. Longiflorine (**25**), isolated from the leaves of *Uncaria longiflora* var. *Pteropoda* (Rubiaceae), is a monoterpenoid alkaloid with a lactam ring derived from secologanin [26]. Lomatogonin C (**26**), isolated from dried whole plants of *Lomatogonium carinthiacum* (Gentianaceae), is a natural monoterpene alkaloid derived from secoiridoid [25].

2.2. Sesquiterpene Alkaloids (27–32)

Sesquiterpene alkaloids represent the least abundant class of TeAs derived from sesquiterpenes and incorporate nitrogen atoms in the basic skeleton of sesquiterpenes [27]. This subsection mainly describes six sesquiterpene alkaloids from nature, including a rare alkaloid from the ocean. The plant sources are listed in Table 2, and the chemical structure details are shown in Figure 2.

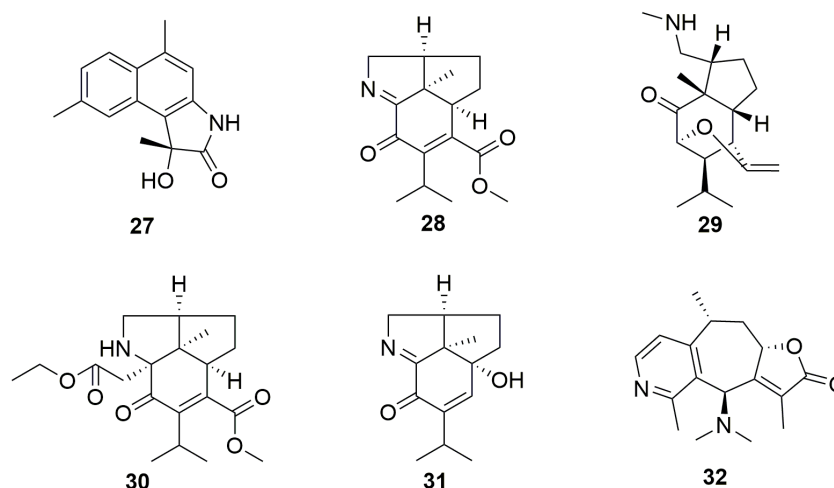


Figure 2. Structures of sesquiterpene alkaloids (27–32).

Table 2. Names and plant sources of sesquiterpene alkaloids (27–32).

No.	Compound Name	Sources	Plant Parts	Ref.
27	Commipholactam A	<i>Resina Commiphora</i>	myrrh	[28]
28	Dendrofindline A	<i>Dendrobium findlayanum</i>	stem	[29]
29	Dendrofindline B	<i>Dendrobium findlayanum</i>	stem	[29]
30	Findlayine D	<i>Dendrobium findlayanum</i>	stem	[30]
31	Findlayine F	<i>Dendrobium findlayanum</i>	stem	[30]
32	Echinoflorine	gorgonian <i>Echinogorgia flora</i>	/	[31]

/: did not report.

Commipholactam A (27) was isolated from the dried myrrh of *Resina Commiphora* and represented a rare cadinane-type sesquiterpenoid. Unlike typical cadinane sesquiterpenoids, where ring C is usually present as a lactone, compound 27 appears as a lactam ring [28].

Dendrofindlines A–B (28–29) and Findlayines D–F (30–31) were all obtained from the dried stems of *Dendrobium findlayanum* and belong to the dendrobine-type alkaloid group [29,30]. Notably, Dendrofindline A (28) and Findlayine D (30) belong to the *sec*-lactone dendrobine-type alkaloid group. Findlayine D (30) is the first reported dendrobine-type alkaloid to feature a 2-ethoxy-2-oxoethyl group attached at C-2. Moreover, Dendrofindline B (29) is identified as a dendrobine-type alkaloid with a nitrogen-containing ring cleavage [29]. Findlayine F (31) is a nor-dendrobine-type alkaloid with a 5-decarboxylated structure [30].

Echinoflorine (32), isolated from the Gorgonian *Echinogorgia flora*, is a guaipyridine-type alkaloid with a γ -lactone-cyclohepta[c]pyridine skeleton, which is different from the cyclohepta[b]pyridine skeleton derived from terrestrial organisms [31].

2.3. Diterpenoid Alkaloids (DAs) (33–289)

DAs are the most abundant and structurally complex TeAs, characterized by numerous stereocenters. They typically originate from the amination of tetracyclic or pentacyclic diterpenes, forming heterocyclic systems possessing β -aminoethanol, methylamine, or ethylamine nitrogen atoms [32]. Based on the number of carbon atoms in the skeleton

of DAs, they can be classified into three major categories: C18, C19, and C20 [33]. Shen Yong comprehensively reviewed the classification of diterpenoid alkaloids in 2020 [8]. Consequently, this article will not delve into an extensive discussion of this classification but will focus only on the classification of new members discovered in the past five years. This section describes 257 newly discovered natural DAs, including 11 C18-DAs, 139 C19-DAs, 84 C20-DAs, 14 Bis-DAs, and 9 other types of DAs. These DAs were predominantly isolated from the plants in the *Aconitum* and *Delphinium* genera, with only two new DAs isolated from the ripe fruits of *Forsythia suspensa*. Additionally, five new DAs were obtained from microorganisms and marine animals.

2.3.1. C18-DAs (33–43)

Without C18 in the structure, these alkaloids predominantly feature a 4-OH or ester substitution, with a few compounds having 3,4-epoxy substitution. According to the presence or absence of oxygen-containing groups at C7, they are classified into lappaconitines and ranaconitines [32]. Eleven C18-DAs (33–43) are described in this subsection. Plant sources are shown in Table 3. Detailed chemical structures are shown in Figure 3.

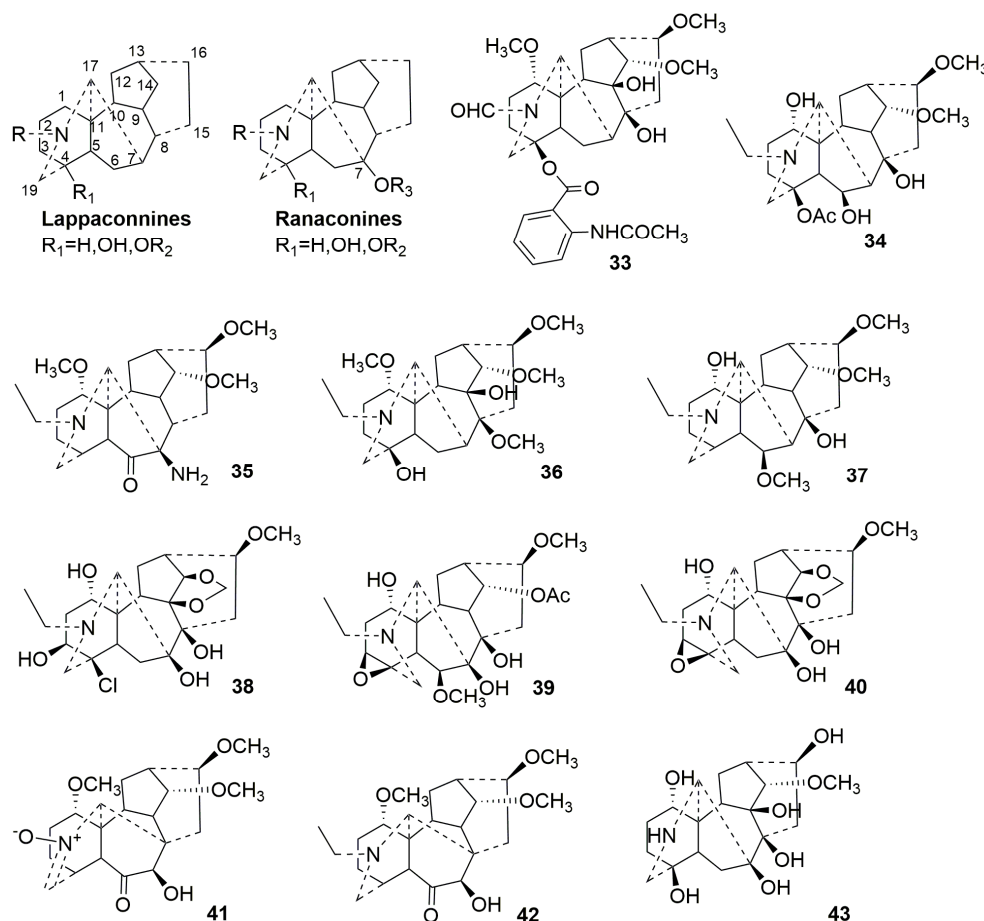


Figure 3. Structures of C18-DAs (33–43).

Compounds 33–37 are identified as lappaconine-type alkaloids, with four originating from *Aconitum* and only Naviconine (33) derived from *Delphinium* [34–36]. Amino groups are generally uncommon in DAs, whereas Leucostosine C(35) is the first naturally occurring DA to feature an amino group attached at C-7 [36].

Compounds 38–40, obtained from *Aconitum*, are classified as ranaconitine-type DAs. Kirisine A (40) and B (38) are rare DAs with 9,14-methylenedioxy group. In addition, kirisine B (38), containing a chlorine substituent at C-4, represents a fourth example of DAs with a chlorine substituent [35].

Compounds **41** and **42** are rearranged C18-DAs, where the C7-C17 bond was rearranged to a C8-C17 bond [37]. Compounds **41** and **42** are derived from the rearrangement of ranaconitine-type DAs, and both contain an oxygen-containing hydroxyl group at C7. Additionally, Barpubenine A (**41**) is the first reported N-oxide in C18-DAs [37].

1-N-deethyl-1,16-demethoxy-1,16-dihydroxypyranaconidine(**43**) is a C18-nor-diterpene alkaloid with a skeleton similar to ranaconidine except that it lacks an N-ethyl group [38]. Furthermore, a hydroxyl group exists at C-16 instead of a methoxy group, which is common in C18-DAs [38].

Table 3. Names and plant sources of C18-DAs (**33–43**).

No.	Compound Name	Sources	Plant Parts	Ref.
33	Naviconine	<i>Delphinium naviculare</i> var. <i>lasiocarpum</i>	whole plant	[34]
34	Kirisine E	<i>Aconitum kirinense</i> Nakai	root	[35]
35	Leucostosine C	<i>Aconitum leucostomum</i> Worosch	root	[36]
36	Leucostosine D	<i>Aconitum leucostomum</i> Worosch	root	[36]
37	Kirisine D	<i>Aconitum kirinense</i> Nakai	root	[35]
38	Kirisine B	<i>Aconitum kirinense</i> Nakai	root	[35]
39	Kirisine C	<i>Aconitum kirinense</i> Nakai	root	[35]
40	Kirisine A	<i>Aconitum kirinense</i> Nakai	root	[35]
41	Barpubenine A	<i>Aconitum barbatum</i> var. <i>puberulum</i> Ledeb.	whole plant	[37]
42	Barpubenine B	<i>Aconitum barbatum</i> var. <i>puberulum</i> Ledeb.	whole plant	[37]
43	1-N-deethyl-1,16-demethoxy-1,16-dihydroxypyranaconidine	<i>Aconitum iochanicum</i> Ledeb.	root	[38]

2.3.2. C19-DAs (**44–182**)

C19-DAs are the largest class of DAs. According to the differences in the skeleton, they can be divided into six types: aconitines, lycoctonines, lactones, 7,17-seco, franchetines, and rearranged class [39]. Aconitines and lycoctonines constitute the majority of C19-DAs. This subsection summarizes 139 new C19-DAs discovered in the past five years, including 70 aconitine-type C19-DAs, 40 lycoctonine-type C19-DAs, 5 lactone-type C19-DAs, 10 franchetine-type C19-DAs, 7 Seco-type C19-DAs, and 7 rearranged C19-DAs.

• Aconitine-type C19-DAs (**44–113**)

Aconitine-type C19-DAs are alkaloids characterized by the absence of an oxygen group at C-7. When ester groups are present at C-8 and C-14, they exhibit acute toxicity [8]. In the past five years, 70 new compounds (**44–113**) were discovered, with 65 obtained from *Aconitum* and 5 from *Delphinium* [32,34,38,40–54]. The compounds were further discussed according to the presence of oxygen-containing groups connected at C-3, C-6, or C-15 positions. The plant sources are shown in Table 4. Detailed chemical structures are shown in Figure 4.

Compounds **44–91** are alkaloids that lack oxygen-containing groups at C-3, C-6, and C-15. Notably, compounds **50–57**, featuring a double bond between the N and C-19, were isolated from *Aconitum* [38,40,50]. Compounds **58–64** are linked to a 2-(2-methyl-4-oxoquinazolin-3-yl) benzoate moiety at C-18 [49,54]. Compounds **58–63** exhibit rotational isomerism due to an unusual axial chiral phenyl-quinoline side chain at C-18, with the stereoisomerism studied by temperature-varying NMR techniques [49,54]. Compounds **68** and **69** have an unusual ketone group attached to C-19, with compound **68** uniquely featuring a ketone group at C-14 instead of a common methoxy or ester group. Compounds **79–84** are new C19-DAs with a vaginatunine A fragment at C-18 [32,55]. Compounds **89–91** lack a common methoxy group in DAs at C-16; however, there is a double bond between C-15 and C-16 [45,46,51].

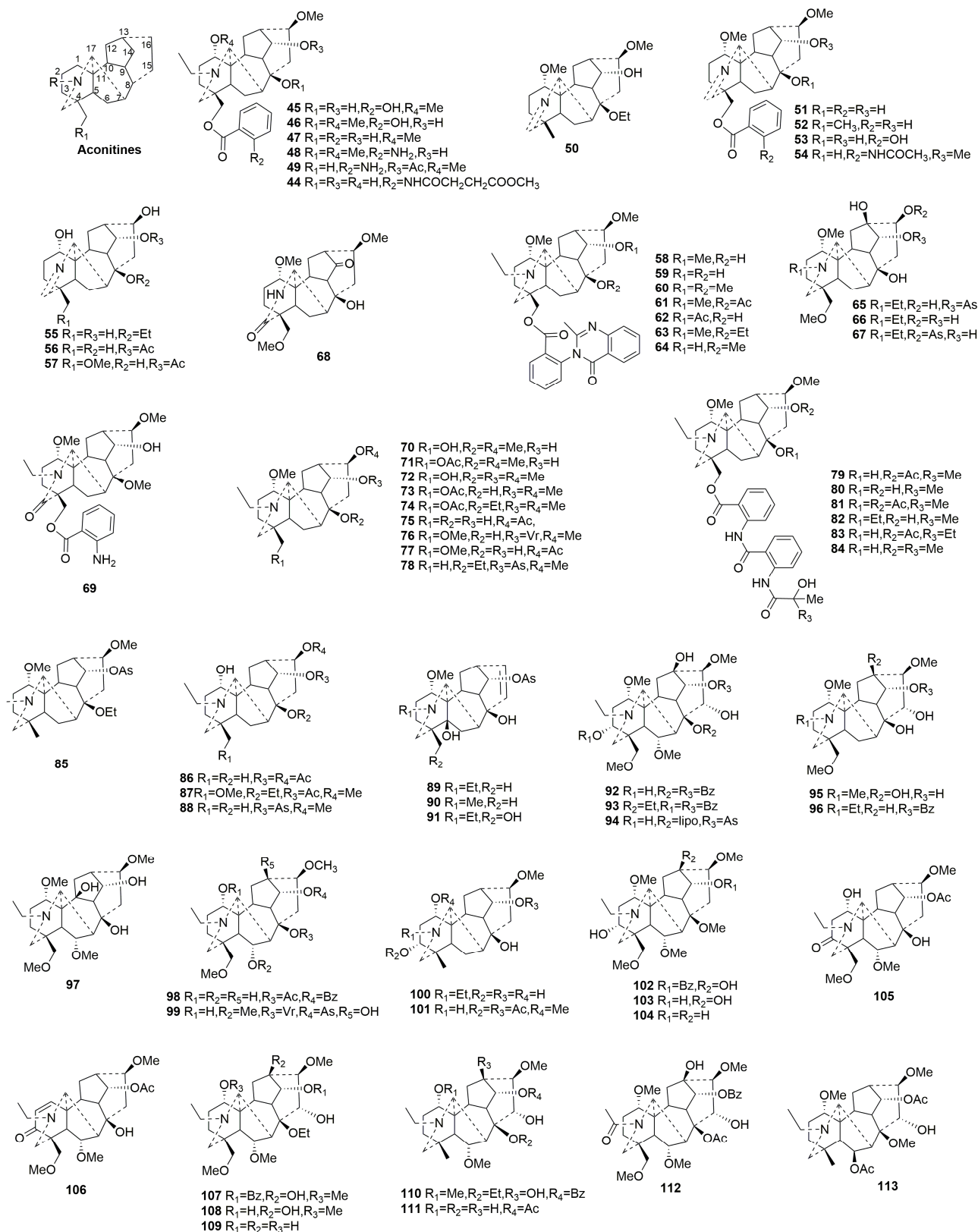


Figure 4. Structures of aconitine-type C19-DAs (44–113).

Compounds **92–94** possess oxygen-containing groups at C-3, C-6, and C-15 [48,56,57]. Interestingly, compound **94** is the third reported C19-DA with hydroxyl groups at C-3, C-13, and C-15 and with a fatty acid ester moiety at C-8 [57]. Compounds **95–96** have hydroxyl groups at C-15 without oxygen-containing groups at C-3/C-6. Compounds **97–99**

are DAs with oxygen-containing groups at C-6, while there are no oxygen-containing groups at C-3 and C-15. Compounds **100–101** have oxygen groups at C-3 but no oxygen groups at C-6 and C-15. Compounds **102–106** have oxygen-containing groups at C-3 and C-6, whereas **105** and **106** contain a ketone group at C-3 [42,48,58]. Compounds **107–113** have oxygen-containing groups at C-6 and C-15 but no oxygen-containing group at C-3 [59]. Interestingly, the acetyloxy group of compound **113** at the C-6 position is β -oriented, uncommon in aconitine-type DAs [48,59].

Table 4. Names and plant sources of aconitine-type C19-DAs (**44–113**).

No.	Compound Name	Sources	Plant Parts	Ref.
44	Naviconitine	<i>Delphinium naviculare</i> var. <i>lasiocarpum</i>	whole plant	[34]
45	Acoapetaludine D	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
46	Acoapetaludine E	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
47	Acoapetaludine F	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
48	Acoapetaludine G	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
49	Forrestline D	<i>Delphinium forrestii</i> var. <i>viride</i>	whole herb	[53]
50	Episcopaline C	<i>Aconitum episcopale</i>	root	[50]
51	Acoapetaludine H	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
52	Acoapetaludine I	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
53	Acoapetaludine J	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
54	Novolunine C	<i>Aconitum novoluridum</i>	root	[49]
55	Austroyunnanine C	<i>Aconitum austroyunnanense</i>	root	[45]
56	1-N-deethyl-1,16-demethoxy-1,16-dihydroxy-N(19)-en-austroconitine A	<i>Aconitum iochanicumone</i>	root	[38]
57	1-N-deethyl-1,16-demethoxy-1,16-dihydroxy-18-methoxy-N(19)-en-austroconitine A	<i>Aconitum iochanicumone</i>	root	[38]
58	Brevicanine A	<i>Aconitum brevicalcaratum</i>	root	[54]
59	Novolunine A	<i>Aconitum novoluridum</i>	root	[49]
60	Novolunine B	<i>Aconitum novoluridum</i>	root	[49]
61	Brevicanine B	<i>Aconitum brevicalcaratum</i>	root	[54]
62	Brevicanine C	<i>Aconitum brevicalcaratum</i>	root	[54]
63	Brevicanine D	<i>Aconitum brevicalcaratum</i>	root	[54]
64	Forrestline B	<i>Delphinium forrestii</i> var. <i>viride</i>	whole herb	[53]
65	Refractine A	<i>Aconitum refractum</i> var. <i>circinatum</i>	whole plant	[41]
66	Richardsonine B	<i>Aconitum richardsonianum</i> Lauener	root	[44]
67	Richardsonine C	<i>Aconitum richardsonianum</i> Lauener	root	[44]
68	Richardsonine A	<i>Aconitum richardsonianum</i> Lauener	root	[44]
69	Acoapetaludine K	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
70	Acoapetaludine B	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
71	Acoapetaludine C	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]
72	Forrestline E	<i>Delphinium forrestii</i> var. <i>viride</i>	whole herb	[53]
73	Brevicalcarine B	<i>Aconitum brevicalcaratum</i>	root	[60]
74	Brevicalcarine C	<i>Aconitum brevicalcaratum</i>	root	[60]
75	Rockidine A	<i>Aconitum genera</i>	root	[43]
76	Pseudostapine A	<i>Aconitum pseudostapfianum</i>	root	[51]
77	Refractine B	<i>Aconitum refractum</i> var. <i>circinatum</i>	whole plant	[41]
78	Austroyunnanine A	<i>Aconitum austroyunnanense</i>	root	[45]
79	Apetalrine A	<i>Aconitum apetalum</i>	aerial part	[55]
80	Apetalrine B	<i>Aconitum apetalum</i>	aerial part	[55]
81	Apetalrine C	<i>Aconitum apetalum</i>	aerial part	[55]
82	Apetalrine D	<i>Aconitum apetalum</i>	aerial part	[55]
83	Apetalrine E	<i>Aconitum apetalum</i>	aerial part	[55]

Table 4. Cont.

No.	Compound Name	Sources	Plant Parts	Ref.
84	Brevicalcarine A	<i>Aconitum brevicalcaratum</i>	root	[60]
85	Nagarumine A	<i>Aconitum nagarum</i>	root	[46]
86	Nagarutine A	<i>Aconitum nagarum</i> Stapf	root	[42]
87	Episcopaline A	<i>Aconitum episcopale</i>	root	[50]
88	Pseudostapine B	<i>Aconitum pseudostapfianum</i>	root	[51]
89	Pseudostapine C	<i>Aconitum pseudostapfianum</i>	root	[51]
90	Nagarumine B	<i>Aconitum nagarum</i>	root	[46]
91	Austroyunnanine B	<i>Aconitum austroyunnanense</i>	root	[45]
92	Smirnotine A	<i>Aconitum smirnovii</i> Steinb	aerial part	[58]
93	Pendulumine A	<i>Aconitum pendulum</i>	rhizome	[48]
94	Lipojesaconitine	<i>Aconitum japonicum</i> subsp. <i>subcuneatum</i>	rhizoma	[57]
95	6-demethoxyhypoconine	<i>Aconitum carmichaelii</i> Debx.	lateral root	[47]
96	Carmichaeline K	<i>Aconitum carmichaelii</i> Debx.	lateral root	[47]
97	10-hydroxychasmanine	<i>Aconitum japonicum</i> subsp. <i>subcuneatum</i>	rhizoma	[57]
98	Rockidine B	<i>Aconitum genera</i>	root	[43]
99	Geordine	<i>Aconitum georgei</i> Comber	root	[61]
100	3-hydroxykaracoline	<i>Aconitum japonicum</i> subsp. <i>subcuneatum</i>	rhizoma	[57]
101	Episcopine B	<i>Aconitum episcopale</i>	root	[52]
102	Acotarine F	<i>Aconitum taronense</i>	root	[56]
103	Acotarine G	<i>Aconitum taronense</i>	root	[56]
104	Smirnotine B	<i>Aconitum smirnovii</i> Steinb	aerial part	[58]
105	Pendulumine E	<i>Aconitum pendulum</i>	rhizome	[48]
106	Nagarutine C	<i>Aconitum nagarum</i> Stapf	root	[42]
107	8-O-ethyl-benzoyldeoxyaconine	<i>Aconitum carmichaelii</i> Debx.	lateral root	[47]
108	Pendulumine C	<i>Aconitum pendulum</i>	rhizome	[48]
109	Pendulumine D	<i>Aconitum pendulum</i>	rhizome	[48]
110	Nagarutine B	<i>Aconitum nagarum</i> Stapf	root	[42]
111	Nagarutine D	<i>Aconitum nagarum</i> Stapf	root	[42]
112	Pendulumine F	<i>Aconitum pendulum</i>	rhizome	[48]
113	Delcarpum	<i>Delphinium peregrinum</i> L. var. <i>eriocarpum</i> Boiss	aerial part	[59]

- Lycoctonine-type C19-DAs (114–153)

Lycoctonine-type C19-DAs are oxidized at C-7 and C-8. Compounds 114–153 are all novel members of the lycoctonine-type C19-DAs, with 38 compounds derived from *Delphinium* and only 2 from *Aconitum* [62–68]. The plant sources are shown in Table 5. Detailed chemical structures are shown in Figure 5.

According to the different oxygen-containing groups at C-7 and C-8, they can be divided into two subtypes. Eleven new compounds (115–125) feature a C-7 and C-8 diol. Compounds 114 and 126 have rare methoxy and acetoxy groups at C-8, respectively [34,69]. Compounds 115 and 116, isolated from *Aconitum sczukanii*, have very similar chemical structures, with the only difference being the presence of double bonds between C-2 and C-3 in compound 115 [65]. Compound 117 contains a carboxyl group attached to the nitrogen. Compounds 118 and 119 are identified as a pair of regioisomers [62]. Compound 121 from *Delphinium ajacis* is notable for its rare hydroxyl group at C-12 [70]. Compounds 124–126 all featured a characteristic N=CH fragment, with compound 126 also possessing an additional nitrone group [68].

Twenty-seven novel compounds (127–153) obtained from *Delphinium* species all have a 7,8-methylenedioxy group. Compounds 130 and 131 each have a rare aldehyde group attached to the N atom [67]. Compound 145 is unprecedented, with an ether bond between C-1 and C-19 [71]. Compounds 134, 138, and 153 have an N=CH fragment, with compounds 138 and 153 further possessing a nitrone group [64,67,72]. Compounds 136–137 and 149–152 have a characteristic keto group attached to C-19 [67,72]. Interestingly, compound 153 from *Delphinium* displays an unusual β -oriented 1-OMe [72].

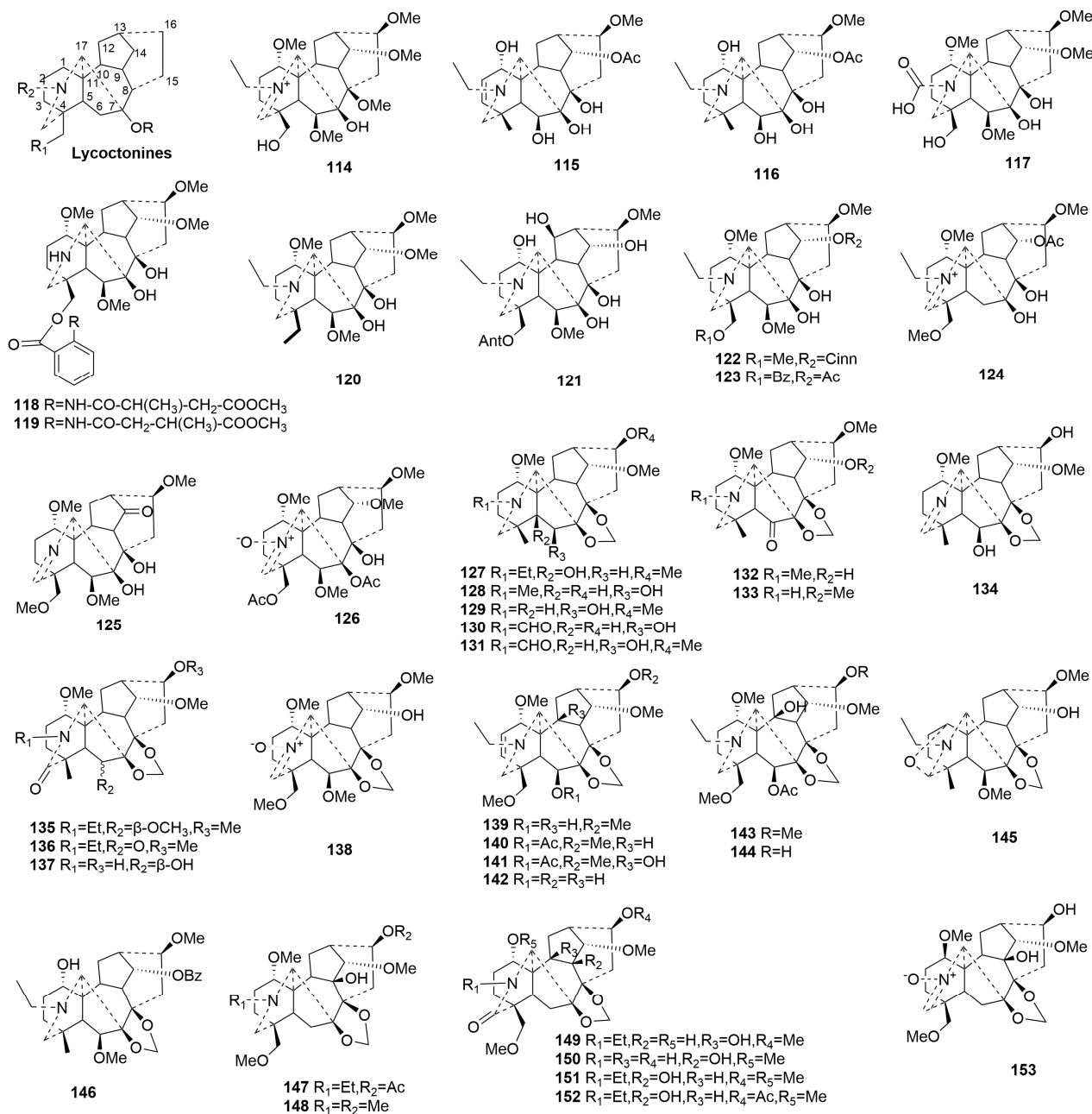


Figure 5. Structures of lycoctonine-type C19-DAs (114–153).

Table 5. Names and plant sources of lycoctonine-type C19-DAs (114–153).

No.	Compound Name	Sources	Plant Parts	Ref.
114	Naviculine	<i>Delphinium naviculare</i> var. <i>lasiocarpum</i>	whole plant	[34]
115	Sczukiniline D	<i>Aconitum sczukinii</i> Turcz	root	[65]
116	Sczukiniline E	<i>Aconitum sczukinii</i> Turcz	root	[65]
117	Grandifline C	<i>Delphinium grandiflorum</i>	aerial parts	[73]
118	Shawurenine C	<i>Delphinium shawurense</i> W. T. Wang	aerial parts	[62]
119	Shawurenine D	<i>Delphinium shawurense</i> W. T. Wang	aerial parts	[62]
120	Uncinatine-A	<i>Delphinium uncinatum</i>	whole plant	[66]
121	Ajacinine G	<i>Delphinium ajacis</i>	seed	[70]
122	Grandiflonine F	<i>Delphinium grandiflorum</i> L.	whole plant	[68]
123	Ajacinine F	<i>Delphinium ajacis</i>	seed	[70]

Table 5. Cont.

No.	Compound Name	Sources	Plant Parts	Ref.
124	Grandiflonine E	<i>Delphinium grandiflorum</i> L.	whole plant	[68]
125	Grandiflonine G	<i>Delphinium grandiflorum</i> L.	whole plant	[68]
126	Chrysotrichumine A	<i>Delphinium chrysotrichum</i>	aerial parts	[69]
127	Elapaciline	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
128	Meladine	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
129	N-deethyldepheline	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
130	N-deethyl-N-formyleladine	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
131	N-deethyl-N-formyldepheline	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
132	Melapacitine	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
133	N-deethylpacinine	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
134	Iminoeladine	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
135	19-oxopaciline	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
136	19-oxopacinine	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
137	N-deethyl-19-oxoeladine	<i>Delphinium elatum</i> cv. Pacific Giant	seed	[67]
138	Brunodelphinine C	<i>Delphinium brunonianum</i> Royle	aerial parts	[64]
139	Grandifoline A	<i>Delphinium grandiflorum</i> L.	whole herb	[63]
140	Grandifoline B	<i>Delphinium grandiflorum</i> L.	whole herb	[63]
141	Grandifoline C	<i>Delphinium grandiflorum</i> L.	whole herb	[63]
142	Grandifoline E	<i>Delphinium grandiflorum</i> L.	whole herb	[63]
143	Grandifoline D	<i>Delphinium grandiflorum</i> L.	whole herb	[63]
144	Grandifoline F	<i>Delphinium grandiflorum</i> L.	whole herb	[63]
145	Liangshanine A	<i>Delphinium liangshanense</i> W. T. Wang	whole plant	[71]
146	Liangshanine B	<i>Delphinium liangshanense</i> W. T. Wang	whole plant	[71]
147	Kamaonensine A	<i>Delphinium kamaonense</i> Huth	whole plant	[72]
148	Kamaonensine B	<i>Delphinium kamaonense</i> Huth	whole plant	[72]
149	Kamaonensine C	<i>Delphinium kamaonense</i> Huth	whole plant	[72]
150	Kamaonensine D	<i>Delphinium kamaonense</i> Huth	whole plant	[72]
151	Kamaonensine E	<i>Delphinium kamaonense</i> Huth	whole plant	[72]
152	Kamaonensine G	<i>Delphinium kamaonense</i> Huth	whole plant	[72]
153	Kamaonensine F	<i>Delphinium kamaonense</i> Huth	whole plant	[72]

- Lactone-type C19-DAs (154–158)

Lactone-type C19-DAs are generally formed by oxidation of the 14-ketone in the C ring of aconitine-type DAs to form a six-membered lactone C ring. Only five new members (154–158) belong to this type. The plant sources are shown in Table 6. Detailed chemical structures are shown in Figure 6.

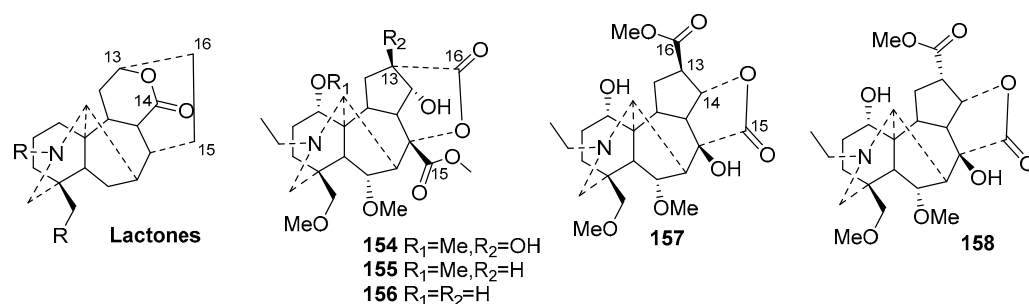


Figure 6. Structures of lactone-type C19-DAs (154–158).

Interestingly, these five newly discovered lactone-type C19-DAs have an unprecedented five-membered lactone D ring [74,75]. Compounds 154–158 are formed by cleavage of the bond between C-15 and C-16, followed by subsequent lactonization. In addition, compounds 157 and 158 are C-13 epimers of each other, highlighting a unique aspect of their structural configuration [74].

Table 6. Names and plant sources of lactone-type C19-DAs (154–158).

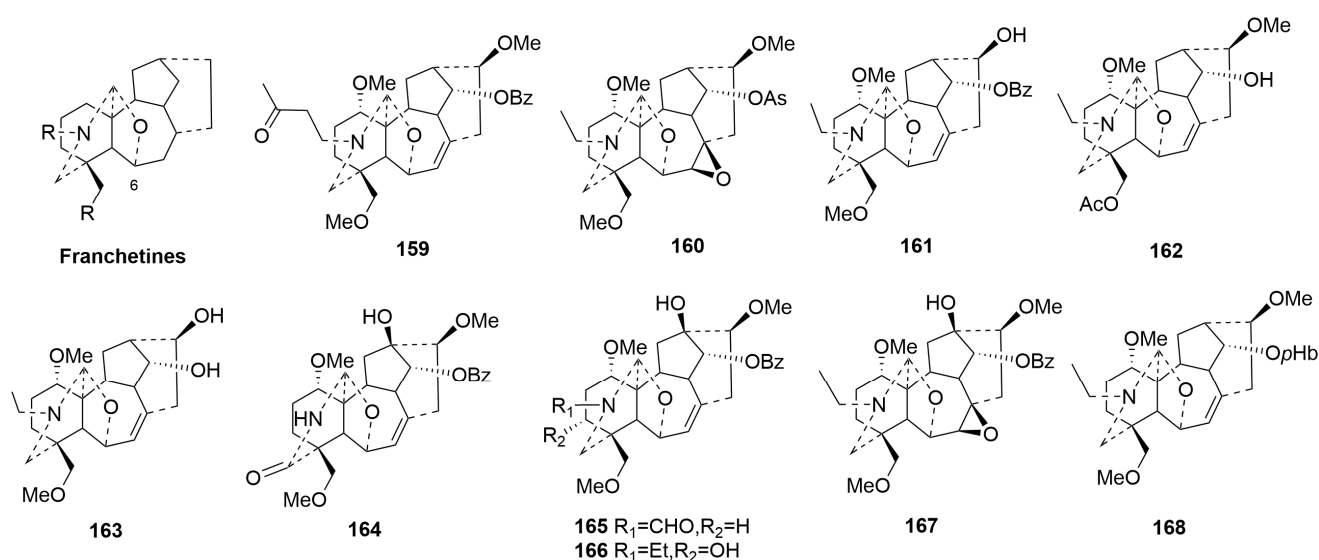
No.	Compound Name	Sources	Plant Parts	Ref.
154	Kusnezosine A	<i>Aconitum kusnezoffii</i> Reichb. var. <i>gibbiferum</i>	root	[75]
155	Kusnezosine B	<i>Aconitum kusnezoffii</i> Reichb. var. <i>gibbiferum</i>	root	[75]
156	Kusnezosine C	<i>Aconitum kusnezoffii</i> Reichb. var. <i>gibbiferum</i>	root	[75]
157	Stylosine A	<i>Aconitum stylosum</i>	root	[74]
158	Stylosine B	<i>Aconitum stylosum</i>	root	[74]

- Franchetine-type C19-DAs (159–168)

Franchetine-type C19-DAs are distinguished from aconitines by an additional ether between C-6 and C-17. Ten novel alkaloids (159–168) are classified as franchetine-type C19-DAs [43,56,76]. The plant sources are shown in Table 7. Detailed chemical structures are shown in Figure 7. Compounds 159, 161–166, and 168 have a double bond between C-7 and C-8, whereas compounds 160 and 167 have a 7,8-epoxy unit [43,56,76]. In addition, Compounds 161 and 163 have a characteristic hydroxyl group at C-16 instead of the methoxy group joint in DAs.

Table 7. Names and plant sources of franchetine-type C19-DAs (159–168).

No.	Compound Name	Sources	Plant Parts	Ref.
159	Acotarine A	<i>Aconitum taronense</i>	root	[56]
160	Acotarine B	<i>Aconitum taronense</i>	root	[56]
161	Acotarine C	<i>Aconitum taronense</i>	root	[56]
162	Acotarine D	<i>Aconitum taronense</i>	root	[56]
163	Acotarine E	<i>Aconitum taronense</i>	root	[56]
164	Flavumoline A	<i>Aconitum flavum</i> Hand.-Mazz	aerial parts	[76]
165	Flavumoline B	<i>Aconitum flavum</i> Hand.-Mazz	aerial parts	[76]
166	Flavumoline C	<i>Aconitum flavum</i> Hand.-Mazz	aerial parts	[76]
167	Flavumoline D	<i>Aconitum flavum</i> Hand.-Mazz	aerial parts	[76]
168	Rockidine C	<i>Aconitum</i> genera	root	[43]

**Figure 7.** Structures of franchetine-type C19-DAs (159–168).

- 7,17-*seco*-type C19-DAs (169–175)

7,17-*seco*-type C19-DAs are characterized by the cleavage of the C7-C17 bond, typically along with double bonds between C-7 and C-8. There are seven members (169–175) of this class that have been identified over the past five years. Interestingly, compounds 169–173

have a hemiacetal fragment, which results from the C7-C17 bond breaking, followed by the formation of an ether bond [64,73,77]. Compounds **169–173** are the 7,17-seco-lycoctonine C19-DAs with a C7-O-C17 unit [73]. Compounds **170–173** have an unprecedented N, O-diacetyl residue [77]. Among them, compounds **170** and **172** are isomers; the methoxy group is located at C-11 in **172** and at C-6 in **170**. Moreover, compound **173**, lacking a methoxy group at C-6, is a demethylation product of **170**. The plant sources are shown in Table 8, and detailed chemical structures are shown in Figure 8.

Table 8. Names and plant sources of 7,17-seco-type C19-DAs (**169–175**).

No.	Compound Name	Sources	Plant Parts	Ref.
169	Grandifline B	<i>Delphinium grandiflorum</i>	aerial part	[73]
170	Aconicumine A	<i>Aconitum taipeicum</i> Hand.-Mazz.	root	[77]
171	Aconicumine B	<i>Aconitum taipeicum</i> Hand.-Mazz.	root	[77]
172	Aconicumine C	<i>Aconitum taipeicum</i> Hand.-Mazz.	root	[77]
173	Aconicumine D	<i>Aconitum taipeicum</i> Hand.-Mazz.	root	[77]
174	Brunodelphinine B	<i>Delphinium brunonianum</i> Royle	aerial part	[64]
175	Brunodelphinine D	<i>Delphinium brunonianum</i> Royle	aerial part	[64]

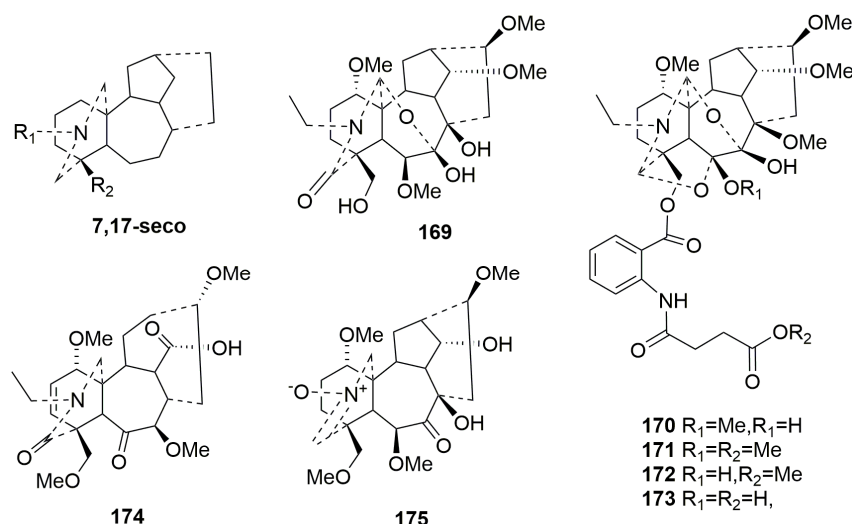


Figure 8. Structures of 7,17-seco-type C19-DAs (**169–175**).

• Rearranged C19-DAs (**176–182**)

Over the past five years, only seven members (**176–182**) have been classified as rearranged C19-DAs [46,52,64,73,78]. Compounds **176** and **182** are unique alkaloids with a rearranged six-membered B ring formed by the C-8 and C-10 linkage [46,50]. Compounds **177** and **178** are two new rare rearranged aconitine-type C19-diterpenoid alkaloids whose C7-C17 bond rearranges to form a C8-C17 bond [79]. The N-C19 and C7-C17 bonds in compound **179** are broken and rearranged into N-C7 bonds, and C-19 was oxidized to carbonyl [73]. In addition, compound **179** belongs to a new rearranged subtype named grandiflodines, which possesses a C7-N-C17 unit and a C17-O-C19 unit. Compound **181** displays an unusual rearranged C19-DA skeleton with the cleavage of N-C19 and C7-C17 bonds and the construction of the N-C7 bond [78]. The plant sources are shown in Table 9. Detailed chemical structures are shown in Figure 9.

Table 9. Names and plant sources of rearranged C19-DAs (176–182).

No.	Compound Name	Sources	Plant Parts	Ref.
176	Nagarumine C	<i>Aconitum nazarum</i>	root	[46]
177	Acosinomonine A	<i>Aconitum sinomontanum</i>	root	[79]
178	Acosinomonine B	<i>Aconitum sinomontanum</i>	root	[79]
179	Grandifline A	<i>Delphinium grandiflorum</i> L.	whole herb	[73]
180	Episcopine A	<i>Aconitum episcopale</i>	root	[52]
181	Gyalanutine A	<i>Delphinium gyalanum</i> C. Marquand & Airy Shaw	whole plant	[78]
182	Episcopaline B	<i>Aconitum episcopale</i>	root	[50]

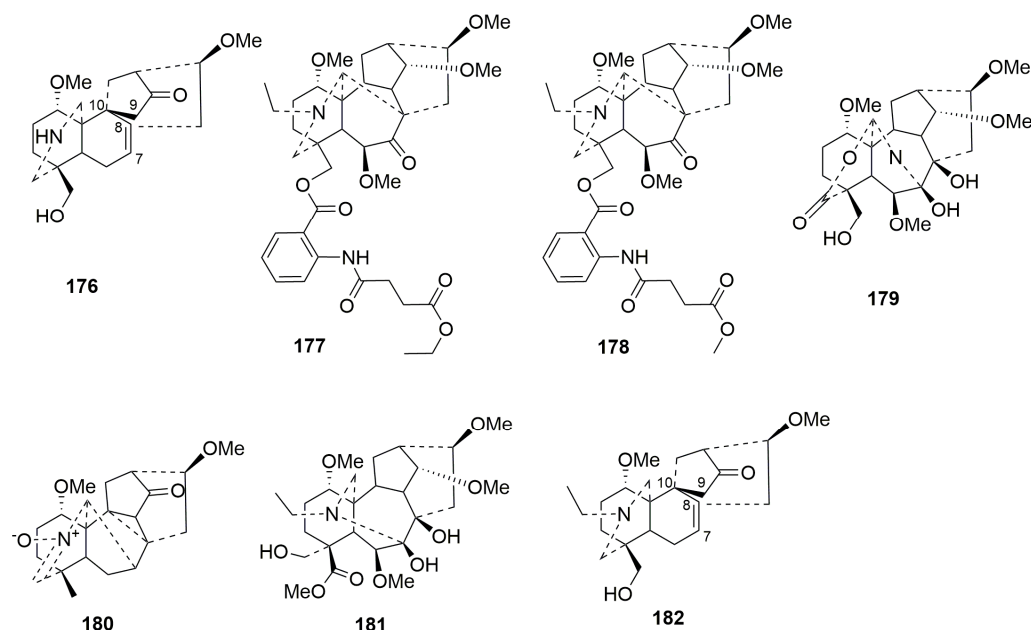


Figure 9. Structures of rearranged C19-DAs (176–182).

2.3.3. C20-DAs (183–266)

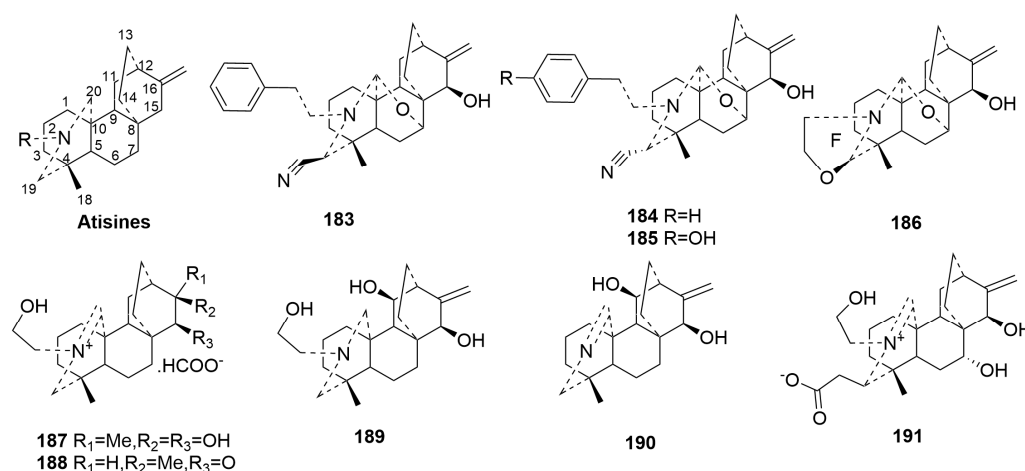
C20-DAs are compounds with structures more complex than those of C18- and C19-DAs, with most C20-DAs having a characteristic exocyclic double bond between C-16 and C-17. Based on the variations in the skeletons, the vast majority of C20-DAs can be classified into seven types: atisines, deudatines, hetisines, hetidines, anopterines, napellines, and vakognavines [39]. This section describes 84 C20-DAs from nature, including 9 atisine-type C20-DAs, 26 hetisine-type C20-DAs, 11 hetidine-type C20-DAs, 13 deudatine-type C20-DAs, 8 napelline-type C20-DAs, 6 vakognavine-type C20-DAs, and 11 rearranged C20-DAs. Among these alkaloids, 62 were obtained from *Aconitum* plants and 22 from *Delphinium* plants.

• Atisine-type C20-DA (183–191)

Atisine-type C20-DAs are structurally characterized by their N atoms being linked to C-20 and C-19 and share the same carbon skeleton as atisine diterpenes. Only nine newly discovered compounds (183–191) have been classified as atisine-type C20-DAs [37,53,69,80,81]. Compounds 183–186, derived from *Delphinium*, feature an additional ether bond between C-20 and C-7. Among these, compounds 183–185 have cyano groups at C-19, making the first reported cyano-containing DAs [80]. Furthermore, compound 186 is noted for bearing an oxazolidine ring F [69]. Compounds 187–188 and 190–191 have a double bond between N and C-20, with compound 188 possessing a rare ketone group at C-15 [37]. The plant sources are shown in Table 10. Detailed chemical structures are shown in Figure 10.

Table 10. Name and plant sources of atisine-type C20-DAs (183–191).

No.	Compound Name	Sources	Plant Parts	Ref.
183	Brunonianine A	<i>Delphinium brunonianum</i> .	whole plant	[80]
184	Brunonianine B	<i>Delphinium brunonianum</i> .	whole plant	[80]
185	Brunonianine C	<i>Delphinium brunonianum</i> .	whole plant	[80]
186	Delphatisine D	<i>Delphinium chrysotrichum</i>	aerial part	[69]
187	Barpubesine A	<i>Aconitum barbatum</i> var. <i>puberulum</i> Ledeb	whole plant	[37]
188	Barpubesine B	<i>Aconitum barbatum</i> var. <i>puberulum</i> Ledeb	whole plant	[37]
189	Barpubesine C	<i>Aconitum barbatum</i> var. <i>puberulum</i> Ledeb	whole plant	[37]
190	Forrestline F	<i>Delphinium forrestii</i> var. <i>viride</i>	whole plant	[53]
191	Brunodelphinine E	<i>Delphinium brunonianum</i>	aerial parts	[64]

**Figure 10.** Structures of atisine-type C20-DAs (183–191).

- Hetisine-type C20-DAs (192–217)

Compared to atisine-type C20-DAs, hetisine-type C20-DAs feature a hexacyclic with an additional C14–C20 bond and N–C6 bond [82]. This category is the largest, and the newly discovered compounds 192–217 belong to this class of C20-DAs [37,59,68,83,84]. Among these, only compound 203, obtained from *Aconitum*, has a hydroxyl group at C-6 [85]. Compounds 204–206 and 211–212 have a hydroxyl group at C-15; notably, only compound 212 shows an α -oriented OH group at C-15 [86]. Compound 210 is the first hetisine-type C20-DA with one hexose substitution, identified as β -glucoside [47]. In addition, Compound 213 is a rare DA linked by the ether bond between C-17' and C-2 between hetisine-type C20-DAs and hetidane-type diterpenes [84]. The plant sources are shown in Table 11. Detailed chemical structures are shown in Figure 11.

Table 11. Names and plant sources of hetisine-type C20-DAs (192–217).

No.	Compound Name	Sources	Plant Parts	Ref.
192	Trichophorine A	<i>Delphinium trichophorum</i> Franch.	whole herb	[83]
193	Trichophorine B	<i>Delphinium trichophorum</i> Franch.	whole herb	[83]
194	Trichophorine C	<i>Delphinium trichophorum</i> Franch.	whole herb	[83]
195	Coreanine A	<i>Aconitum coreanum</i>	root	[87]
196	Coreanine B	<i>Aconitum coreanum</i>	root	[87]
197	Coreanine C	<i>Aconitum coreanum</i>	root	[87]
198	Coreanine D	<i>Aconitum coreanum</i>	root	[87]
199	Tanguticuline A	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[85]
200	Tanguticuline B	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[85]
201	Tanguticuline C	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[85]

Table 11. Cont.

No.	Compound Name	Sources	Plant Parts	Ref.
202	Tanguticuline D	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[85]
203	Tanguticuline E	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[85]
204	Anthoroidine G	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]
205	Anthoroidine H	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]
206	Anthoroidine I	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]
207	Grandiflorine C	<i>Delphinium grandiflorum</i> L.	whole plant	[68]
208	Grandiflorine D	<i>Delphinium grandiflorum</i> L.	whole plant	[68]
209	2-O-cinnamoyl hetisine	<i>Aconitum heterophyllum</i>	root	[88]
210	hetisane-15 β -O- β -D-glucoside	<i>Aconitum carmichaelii</i> Debx.	root	[47]
211	Hydrodavisine	<i>Delphinium peregrinum</i> L. var. <i>eriocarpum</i> Boiss	aerial part	[59]
212	Pachycentine	<i>Delphinium pachycentrum</i> Hemsl	whole herb	[86]
213	Anthoroidine A	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]
214	Ajacisine H	<i>Delphinium ajacis</i>	seed	[70]
215	Tanguticuline F	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[85]
216	Tanguticuline G	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[85]
217	Gyalanunine B	<i>Delphinium gyalanum</i> C. Marquand & Airy Shaw	whole plant	[89]

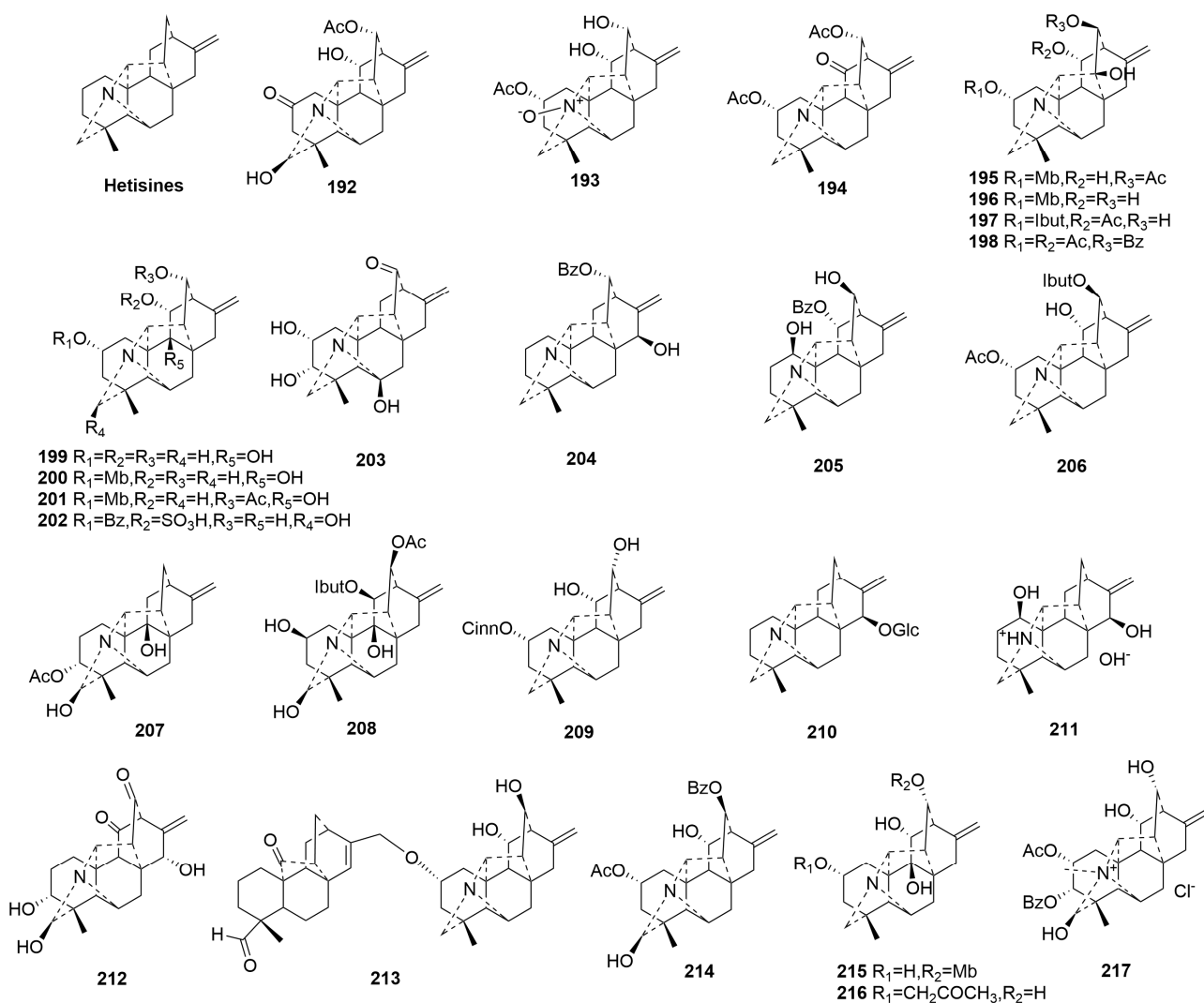


Figure 11. Structures of hetisine-type C20-DAs (192–217).

- Hetidine-type C20-DAs (218–228)

Hetidine-type C20-DAs possess an additional C14–C20 bond, distinguishing them structurally from the atisine class. Eleven new members (218–228) have been classified as such [65,81,84,85,90,91]. Compounds 218–219, 221, 223, and 225–226 all feature a typical exocyclic double bond characteristic of C20-DAs, while compounds 220, 222, and 224 exhibit a distinct intra-ring double bond between C15 and C16. Moreover, compound 226 is notable for having an ester group between C-12 and C-14, forming a lactone ring D, representing a novel skeleton of hetidine-type C20-DAs [65]. The plant sources are shown in Table 12. Detailed chemical structures are shown in Figure 12.

Table 12. Names and plant sources of hetidine-type C20-DAs (218–228).

No.	Compound Name	Sources	Plant Parts	Ref.
218	15-epinaviculine B	<i>Delphinium oreophilum</i>	aerial part	[81]
219	Tangutidine D	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[92]
220	Tangutidine E	<i>Aconitum tanguticum</i> (Maxim.) Stapf	whole plant	[92]
221	Paradoxine	<i>Delphinium paradoxum</i> Bunge	aerial part	[91]
222	Tangutidine A	<i>Aconitum tanguticum</i>	whole plant	[90]
223	Tangutidine B	<i>Aconitum tanguticum</i>	whole plant	[90]
224	Tangutidine C	<i>Aconitum tanguticum</i>	whole plant	[90]
225	Anthoroidine F	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]
226	Sczukiniline A	<i>Aconitum sczukinii</i> Turcz	root	[65]
227	Sczukiniline B	<i>Aconitum sczukinii</i> Turcz	root	[65]
228	Sczukiniline C	<i>Aconitum sczukinii</i> Turcz	root	[65]

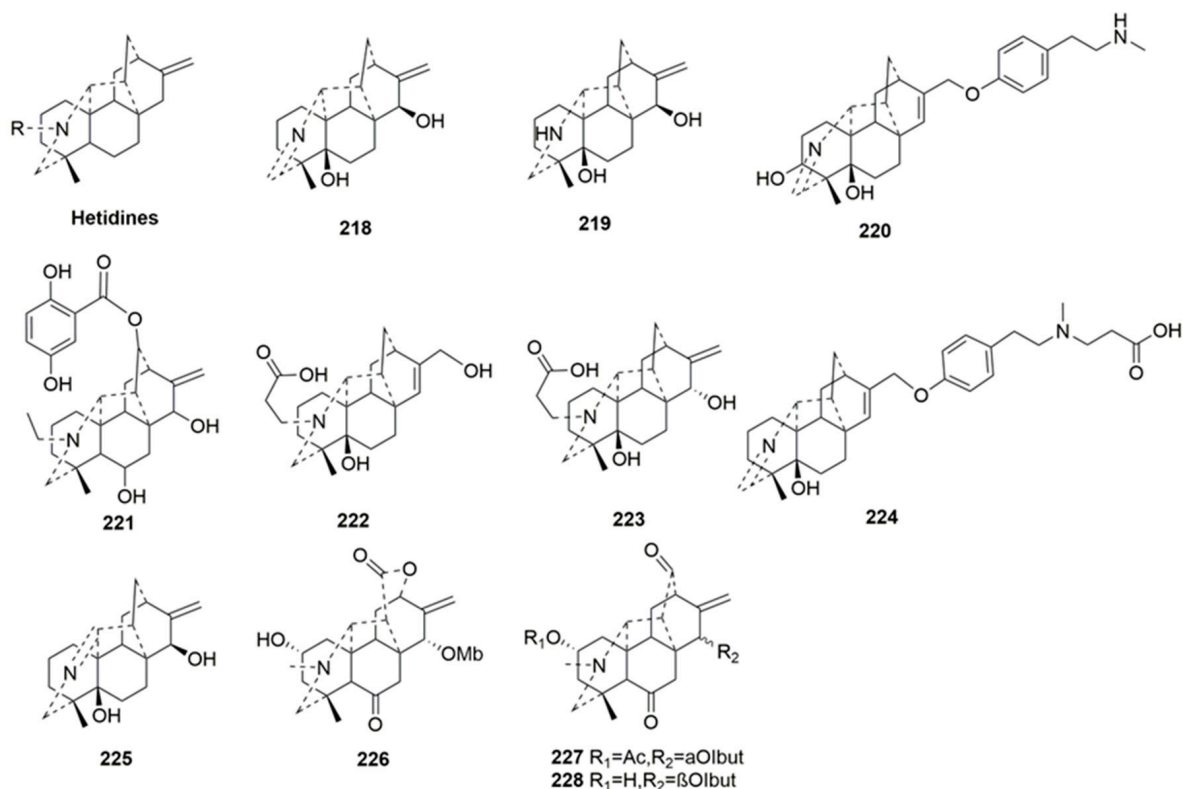


Figure 12. Structures of hetidine-type C20-DAs (218–228).

- Denudatine-type C20-DAs (229–241)

Denudatine-type C20-DAs possess an additional C7–C20 bond compared to the atisine class. Thirteen new compounds (229–241) isolated from the *Aconitum* genus have been classified as this class [35,37,93]. Compounds 229–237 possess typical exocyclic double

bonds between C-16 and C-17, while compounds **238–241** display a hydroxyl group at C-16 and C-17. Compound **233** includes a rare ether bond between C-1 and C-19 [35]. The plant sources are shown in Table 13. Detailed chemical structures are shown in Figure 13.

Table 13. Names and plant sources of denudatine-type C20-DAs (**229–241**).

No.	Compound Name	Sources	Plant Parts	Ref.
229	Kirisine F	<i>Aconitum kirinense</i> Nakai	root	[35]
230	Kirisine G	<i>Aconitum kirinense</i> Nakai	root	[35]
231	Kirisine H	<i>Aconitum kirinense</i> Nakai	root	[35]
232	Kirisine I	<i>Aconitum kirinense</i> Nakai	root	[35]
233	Kirisine J	<i>Aconitum kirinense</i> Nakai	root	[35]
234	Kirisine K	<i>Aconitum kirinense</i> Nakai	root	[35]
235	Kirisine L	<i>Aconitum kirinense</i> Nakai	root	[35]
236	Barpubesine D	<i>Aconitum barbatum</i> var. <i>puberulum</i>	whole plant	[37]
237	Aconicarnine C	<i>Aconitum carmichaelii</i>	lateral root	[93]
238	Aconicarnine A	<i>Aconitum carmichaelii</i>	lateral root	[93]
239	Aconicarnine B	<i>Aconitum carmichaelii</i>	lateral root	[93]
240	Aconicarnine D	<i>Aconitum carmichaelii</i>	lateral root	[93]
241	Aconicarnine E	<i>Aconitum carmichaelii</i>	lateral root	[93]

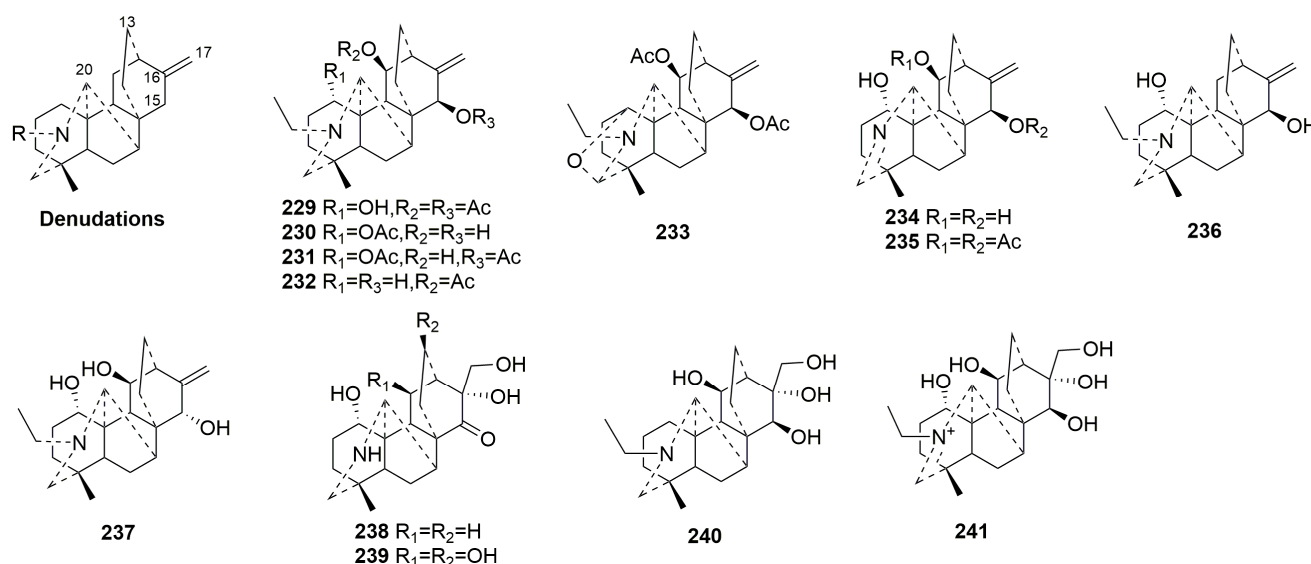


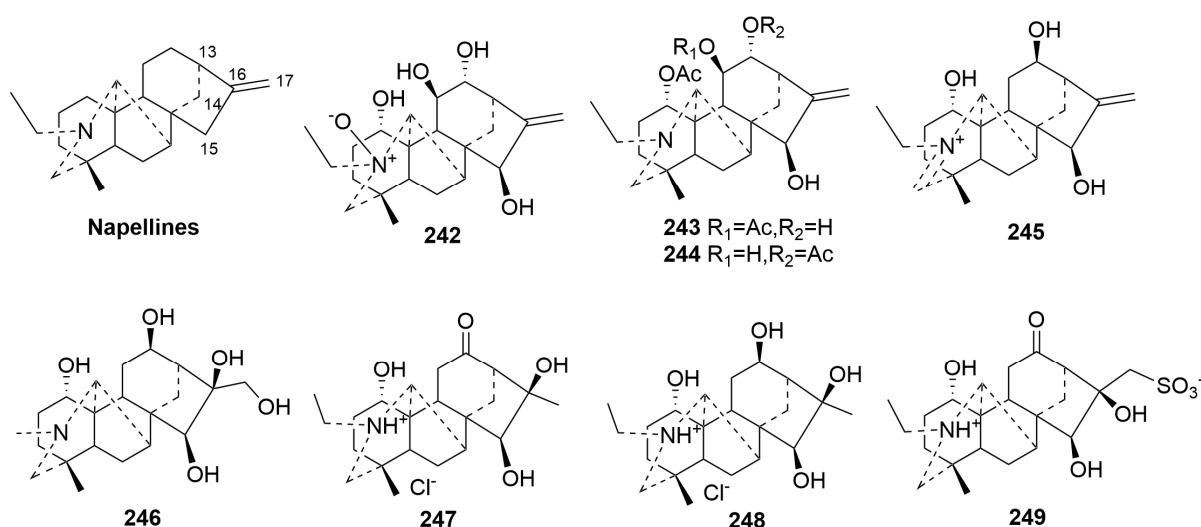
Figure 13. Structures of denudatine-type C20-DAs (**229–241**).

- Napelline-type C20-DAs (**242–249**)

Napelline-type C20-DAs are structurally similar to kaurane diterpenes with the distinctive additional C7-C20 bond. The new compounds **242–249** obtained from the genus *Aconitum* have been classified as this class [35,94–96]. Compounds **242–245** have a typical exocyclic double bond. Among these, compound **242** is a rare N-oxide of natural napelline-type C20-DAs, and compound **245** presents a C20-DA with an iminium methine moiety [35,96]. Compounds **247–248** are napelline-type hydrochloride C20-DAs with a characteristic methyl and hydroxyl group at C-16 instead of a typical exocyclic double bond [94]. Compound **249** contains a sulfonic acid unit [95]. The plant sources are shown in Table 14. Detailed chemical structures are shown in Figure 14.

Table 14. Names and plant sources of napelline-type C20-DAs (242–249).

No.	Compound Name	Sources	Plant Parts	Ref.
242	Kirisine M	<i>Aconitum kirinense</i> Nakai	root	[35]
243	Kirisine N	<i>Aconitum kirinense</i> Nakai	root	[35]
244	Kirisine O	<i>Aconitum kirinense</i> Nakai	root	[35]
245	12-epi-aconicarmichinium A	<i>Aconitum pendulum</i> Busch	root	[96]
246	Napelline C	<i>Aconiti kusnezoffii</i> Radix	root	[94]
247	Napelline D	<i>Aconiti kusnezoffii</i> Radix	root	[94]
248	Napelline E	<i>Aconiti kusnezoffii</i> Radix	root	[94]
249	Chuanfusulfonine A	<i>Aconitum carmichaelii</i>	lateral root	[95]

**Figure 14.** Structures of napelline-type C20-DAs (242–249).

- Vakognavine-type C20-DAs (250–255)

The fundamental skeleton structure of vakognavine-type C20-DAs is defined by the bond cleavage between N and C-19 of hetisines. Only six new compounds (250–255) belong to this class [43,68,89,97]. Compound 253 is the first vakognavine-type C20-DA with a characteristic C2-O-C19 unit. Compounds 254 and 255 represent the first natural diterpenoid alkaloid at C-18, with an α -oriented methyl group [68]. The plant sources are shown in Table 15. Detailed chemical structures are shown in Figure 15.

Table 15. Names and plant sources of vakognavine-type C20-DAs (250–255).

No.	Compound name	Sources	Plant parts	Ref.
250	Rockisine A	<i>Aconitum</i> genera	root	[43]
251	Umbrodine A	<i>Delphinium umbrosum</i> Hand.-Mazz.	whole plant	[97]
252	Kingiadine	<i>Delphinium kingianum</i> Bruhl. ex Huth.	whole plant	[97]
253	Gyalanunine A	<i>Delphinium gyalanum</i> C. Marquand & Airy Shaw	whole plant	[89]
254	Grandiflonine A	<i>Delphinium grandiflorum</i> L.	whole plant	[68]
255	Grandiflonine B	<i>Delphinium grandiflorum</i> L.	whole plant	[68]

- Rearranged C20-DAs (256–266)

Rearranged C20-DAs retain the characteristics of C20-DAs but with altered skeletons. Eleven new compounds (256–266) obtained from *Aconitum* belong to this class [37,40,84,95,98,99]. Compounds 256–258 are rearranged C20-DAs with racemulosine skeletons derived from denudatine-type DAs via double Wanger–Meerwein rearrangements of rings A and C [84]. Compounds 259–260 are zwitterionic sulfonated C20-DAs with a rearranged atisane skeleton. Compounds 261–262 are two sulfonated seco C20-DAs originating from the Criegee

rearrangements; notably, compound **261** is a 13,16-*seco*-napelline DA, and **262** is a 12,13-*seco*-napelline DA [99]. Compounds **263–264** are novel DAs derived through semipinacol rearrangements of the napelline-type DAs, which migrate through C13–C16 and C15–C6 bonds, respectively [95]. Compound **266** has a tetra-hydropyran ring system unlike napellines [40]. The plant sources are shown in Table 16. Detailed chemical structures are shown in Figure 16.

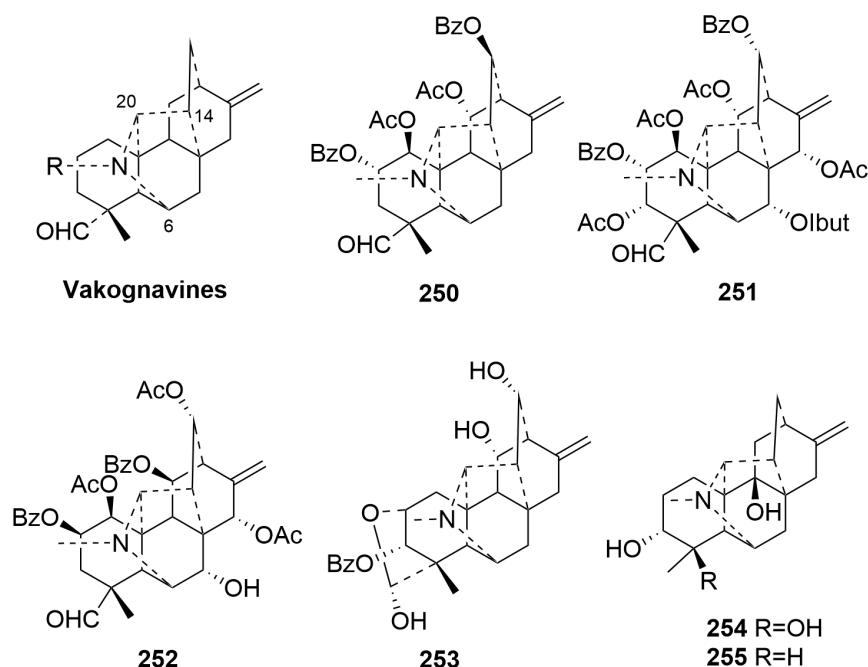


Figure 15. Structures of vakognavine-type C20-DAs (250–255).

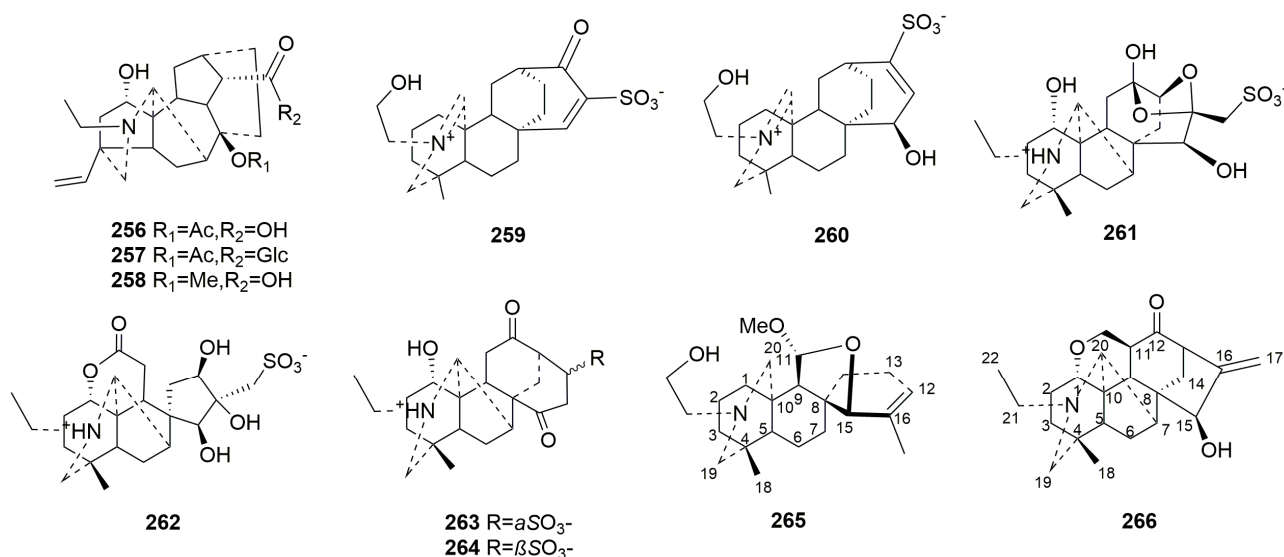


Figure 16. Structures of rearranged C20-DAs (256–266).

Table 16. Names and plant sources of rearranged C20-DAs (256–266).

No.	Compound Name	Sources	Plant Parts	Ref.
256	Anthoroidine C	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]
257	Anthoroidine D	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]
258	Anthoroidine E	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]

Table 16. Cont.

No.	Compound Name	Sources	Plant Parts	Ref.
259	Aconicatisulfonine A	<i>Aconitum carmichaelii</i>	lateral root	[98]
260	Aconicatisulfonine B	<i>Aconitum carmichaelii</i>	lateral root	[98]
261	Aconapelsulfonine A	<i>Aconitum carmichaelii</i>	lateral root	[99]
262	Aconapelsulfonine B	<i>Aconitum carmichaelii</i>	lateral root	[99]
263	Aconicarmisulfonine B	<i>Aconitum carmichaelii</i>	lateral root	[95]
264	Aconicarmisulfonine C	<i>Aconitum carmichaelii</i>	lateral root	[95]
265	Barpuberudine	<i>Aconitum barbatum</i> var. <i>puberulum</i> Ledeb	whole plant	[37]
266	Acoapetaludine A	<i>Aconitum apetalum</i> (Huth) B.Fedtsch	whole plant	[40]

2.3.4. Bis-DAs (267–280)

Bis-DAs are formed by condensing two molecules of diterpenoid alkaloids, typically linked via an O-ether linkage. Fourteen new members (267–280), all obtained from the *Aconitum* plant, have been identified [84,92,100]. The plant sources are shown in Table 17. Detailed chemical structures are shown in Figure 17.

Table 17. Names and plant sources of Bis-DAs (267–280).

No.	Compound Name	Types	Sources	Plant Parts	Ref.
267	Weisaconitine E	denudatine-atisine	<i>Aconitum weixiense</i>	root	[100]
268	Weisaconitine F	denudatine-atisine	<i>Aconitum weixiense</i>	root	[100]
269	Tangirine A	heteratisine-hetidine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
270	Tanguticinine A	hetidine-hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
271	Tanguticinine B	hetidine-hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
272	Tanguticinine C	hetidine-hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
273	Tanguticinine D	hetidine-hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
274	Tanguticinine E	hetidine-hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
275	Tanguticinine F	hetidine-hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
276	Tanguticinine G	hetidine-atisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
277	Anthoroidine B	hetidine-rearranged hetisine	<i>Aconitum anthoroideum</i> DC.	whole plant	[84]
278	N-oxide anthoroidine B	hetidine-rearranged hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
279	5-deoxyanthoridine B	hetidine-rearranged hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]
280	N-oxide 5-deoxyanthoridine B	hetidine-rearranged hetisine	<i>Aconitum tanguticum</i> (Maxim.) Stapf.	whole plant	[92]

Compounds 267–268 are classified as denudatine–atistine-type Bis-DAs, with denudatine and atistine fragments linked by an ether bond between C-17 and C-22' [100]. Compound 269, with heteratisine and hetidine fragments linked by an ether bond between C-17 and C-18', falls into the heteratisine–hetidine class of alkaloids [92]. Compounds 270–275 belong to hetidine–hetisine class, whose hetidine fragments and hetisine fragments are linked by ether bonds [84]. Among these, Compounds 270–274 are isomers, differing only in the position of the hydroxyl substitution in the hetisine moiety [92]. Compounds 277–280, as hetidine-rearranged hetisine-class alkaloids, are bridged by a rare single bond between C-17 and C-17' in Bis-DAs [84,92].

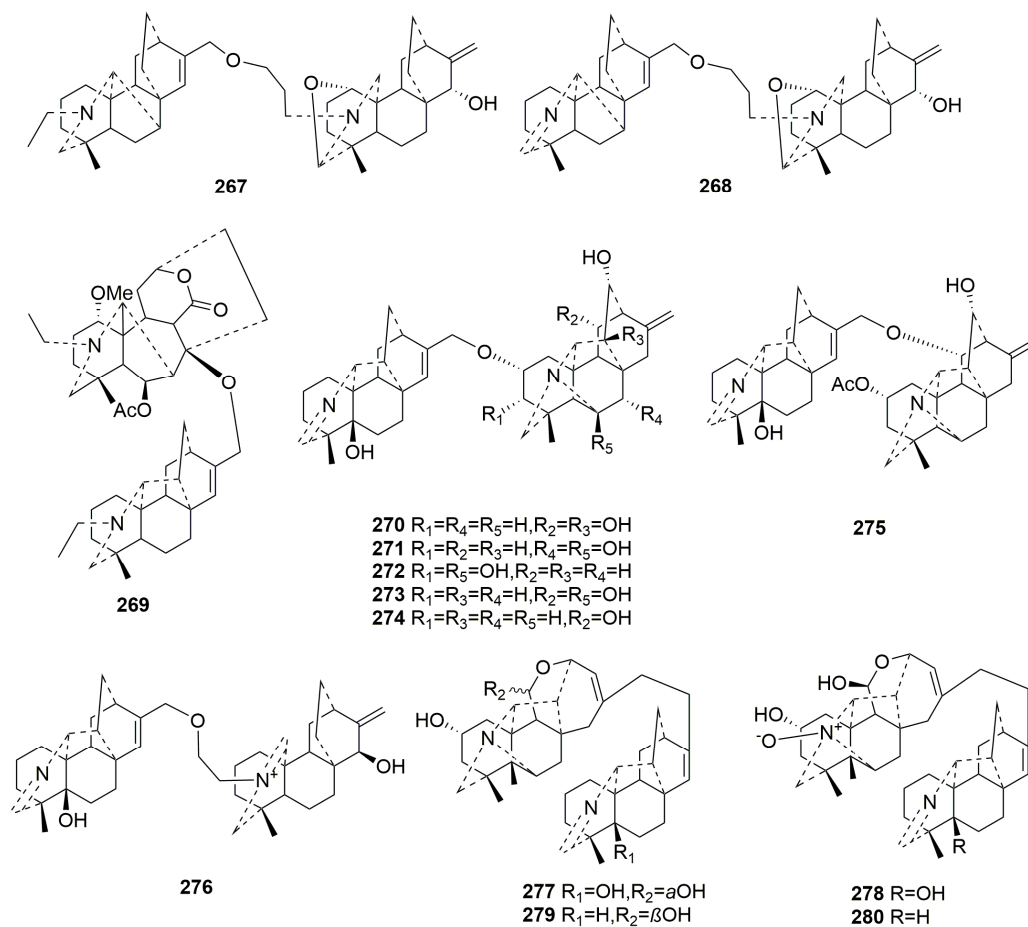


Figure 17. Structures of Bis-DAs (267–280).

2.3.5. Other DAs (281–289)

In addition to the diterpenoid alkaloids mentioned above, some diterpenoid alkaloids have novel structures, such as compounds 281–289 [100–103]. The sources are shown in Table 18. Detailed chemical structures are shown in Figure 18.

Table 18. Names and plant sources of other DAs (281–289).

No.	Compound Name	Sources	Ref.
281	Ceylonamide G	<i>Spongia</i> sp.	[101]
282	Ceylonamide H	<i>Spongia</i> sp.	[101]
283	Ceylonamide I	<i>Spongia</i> sp.	[101]
284	Koninginol A	<i>Trichoderma koningiopsis</i> A729	[102]
285	Koninginol B	<i>Trichoderma koningiopsis</i> A729	[102]
286	Forsyqinlingine A	<i>Forsythia suspensa</i>	[103]
287	Forsyqinlingine B	<i>Forsythia suspensa</i>	[103]
288	Aconidenusulfonine A	<i>Aconitum carmichaelii</i>	[104]
289	12,16-secoaconidenusulfonine A	<i>Aconitum carmichaelii</i>	[104]

Compounds 281–283, isolated from the marine sponge *Spongia* sp., a marine invertebrate, represent three novel DAs with γ -lactam rings [101]. Compounds 284–285 are novel DAs with a guanacastane skeleton isolated from the endophytic fungus *Trichoderma koningii* A729 [102].

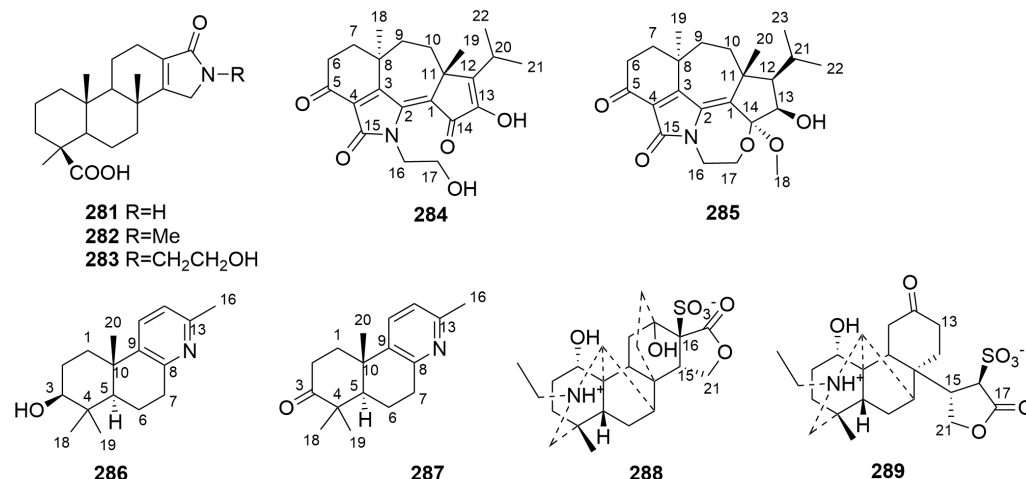


Figure 18. Structures of other DAs (281–289).

Compounds **286–287** are two C₁₇-labdane DAs isolated from ripe fruits of *Forsythia suspensa*. The structure of **286** was determined as 3-hydroxyl-4,4,10,13-tetramethyl-1(2),3(4),5(10),6(7)-octahydrobenzo[*f*]quinolin, and **287** was obtained by oxidation of the hydroxyl group at C-3 in **286** [103]. Compounds **288–289**, isolated from lateral roots of *Aconitum carmichaelii*, represent the first reported natural C₂₁-DAs. The structure of **288** is similar to that of denudatine- and napelline-type C₂₀-DAs. Compound **289** is an isomer of **288**, a 12,16-*seco* derivative of **288** [104].

3. Biological Activity

Terpenoid alkaloids, a class of compounds with far-reaching pharmacological significance, exhibit unique pharmacological effects and extensive biological activities. This section provides an overview of the biological activities of TeAs that have been newly discovered in the past five years, including anti-inflammatory activity, analgesic effect, anticancer activity, and antibacterial and antiviral properties. A table of TeAs' biological activities is provided (Table 19).

3.1. Anti-Inflammatory Activity

The anti-inflammatory activity of TeAs has been well documented, with compounds like gentianine and benzoyleconitine among those reported [105,106]. This paper highlights 16 new anti-inflammatory members in TeAs over the past five years, including 4 monoterpene alkaloids and 12 DAs.

Delavatines C (**9**) and E (**11**) showed more significant inhibition of NO production in lipopolysaccharide (LPS)-stimulated BV2 cells compared to aminoguanidine bicarbonate, with IC₅₀ values of 25.62 and 17.29 μM, respectively, and no cytotoxicity [18]. Stylosine A (**157**) showed significant inhibitory activity against LPS-induced production of inflammatory cytokines (IL-1β, COX-2, and TNF-α) in RAW264.7 cells at a dose of 0.1 μg/mL without cytotoxicity [74]. Geordine (**103**) exhibited specific anti-inflammatory activity and inhibited LPS-induced NO production in RAW264.7 cells at 50 μM, with an inhibition rate of 29.75% [61]. Ajacisines F–H (**121**, **123**, and **214**) showed strong anti-inflammatory activity by inhibiting LPS-induced NO production in BV-2 cells, with inhibition rates of 80% at 50 μM and no cytotoxicity [70]. Anthoroidine B (**277**) inhibited the production of NO and TNF-α, with IC₅₀ values of 357.68 and 67.56 μM, respectively [84].

Forqinlingines C–D (**14–15**) and forsyqinlingines A–B (**286–287**) showed anti-inflammatory activities by inhibiting the release of β-glucuronidase in polymorphonuclear leukocytes (PMNs) induced by platelet-activating factor (PAF), with inhibition rates of 45.2%, 40.1%, 56.7%, and 58.6%, respectively [21].

Table 19. Biological activity of terpenoid alkaloids.

TeAs Types	Activities	Research Method	Possible Mechanism	Ref.
Monoterpenoid Alkaloids				
Alstochonine A (1)	Vasorelaxant	In vitro	Vasorelaxant activity against phenylephrine-induced contraction of rat mesenteric arteries with rates of $73.6 \pm 2.8\%$ and $95.4 \pm 3.7\%$ ($IC_{50} = 93.30 \pm 10.81, 60.56 \pm 3.66 \mu M$)	[16]
Alstochonine B (2)		In vitro		[16]
Delavatine C (9)	Anti-inflammatory	In vitro	Inhibition of NO production in LPS-stimulated BV2 cells ($IC_{50} = 25.62, 17.29 \mu M$)	[18]
Delavatine E (11)		In vitro		[18]
Forsyqinlingine C (14)	Anti-inflammatory and antiviral	In vitro	Anti-inflammatory activities by inhibiting the release of β -glucuronidase in PMNs with inhibition rates of 45.2% and 40.1%, and antiviral activities against H1N1 virus ($IC_{50} = 11.9, 15.1 \mu M$) and RSV ($EC_{50} = 13.5, 14.0 \mu M$)	[21]
Forsyqinlingine D (15)		In vitro		[21]
Incarvine G (12)	Antitumor	In vitro	Cytotoxicity ($IC_{50} = 60.29 \mu M$) against MDA-MB-231 cells and inhibiting actin cytoskeleton formation	[19]
($\pm$)-Caryopterisine A (19)		In vitro	Reduction of Kyn biosynthesis in HeLa cells by inhibiting IDO at 10 μM with inhibition ratios of 25.7% and 29.8%, respectively	[22]
($\pm$)-Caryopterisine B (20)		In vitro		[22]
Caryopterisine C (16)	Antifibrotic	In vitro	Inhibition of collagen accumulation ($IC_{50} = 14.26 \pm 1.46 \mu M$) in NIH3T3 cells and phosphorylation of ERK1/2, P38, and SMAD2/3	[23]
Lomatogonin C (26)	Immunosuppressive	In vitro	Inhibition of T cell proliferation ($21.62 \pm 3.06\%$) and IFN- γ secretion ($37.59 \pm 5.41\%$) at 20 μM	[26]
Sesquiterpene alkaloids				
Commipholactam A (27)	Antitumor	In vitro	Cytotoxicity against HepG2 ($IC_{50} = 21.73 \pm 2.86 \mu M$) and A549 ($IC_{50} = 128.50 \pm 17.06 \mu M$) cells	[28]
Diterpenoid alkaloids				
Geordine (103)	Anti-inflammatory	In vitro	Inhibition of NO production (29.75%) in LPS-induced RAW264.7 cells at 50 μM	[61]
Stylosine A (157)		In vitro	Inhibition of production of IL-1 β , COX-2, and TNF- α in LPS-induced RAW264.7 cells in a dose-dependent manner	[74]
Ajacisine F (121)		In vitro	Inhibition of NO production in LPS-induced BV-2 cells with inhibition rates of 80% at 50 μM	[70]
Ajacisine G (123)		In vitro		[70]
Ajacisine H (214)		In vitro		[70]
Kamaonensine B (148)		In vitro	Inhibition of NO production in LPS-stimulated RAW264.7 cells ($IC_{50} = 2.7 \pm 0.5$ and $0.9 \pm 0.2 \mu M$) and might be mediated by the regulation of some related proteins in the MAPK signaling pathways	[72]
Kamaonensine F (153)		In vitro		[72]
Aconicumine A (170)		In vitro	Inhibition of LPS-activated NO production in RAW264.7 cells ($IC_{50} = 19.7 \pm 1.1 \mu M$)	[77]
Forrestline F (190)		In vitro	Inhibition of NO production in RAW264.7 cells ($IC_{50} = 9.57 \pm 1.34 \mu M$) through inhibiting NF- κB , MAPK, and Nrf2 signaling pathways	[53]
Anthoroidine B (277)		In vitro	Inhibition of the production of NO and TNF- α in LPS-stimulated RAW264.7 cells, with IC_{50} values of 357.68 and 67.56 μM	[84]

Table 19. Cont.

TeAs Types	Activities	Research Method	Possible Mechanism	Ref.
Forsyqinlingine A (286)	Anti-inflammatory and antiviral	In vitro	Anti-inflammatory activities by inhibiting the release of β -glucuronidase in PMNs with inhibition rates of 56.7 and 58.6%, and antiviral activities against H1N1 virus (IC_{50} = 6.9 and 7.7 μ M) and RSV (EC_{50} = 5.0 and 4.8 μ M)	[103]
Forsyqinlingine B (287)		In vitro		[103]
Pseudostapine C (89)	Analgesic	In vivo	Reduction of acetic acid-induced abdominal contractions in mice in a dose-related manner, with the ID_{50} values of 66.1, 60.3, 48.0, and 55.0 μ mol/kg, respectively	[51]
Austroyunnanine B (91)		In vivo		[45]
Episcopine A (180)		In vivo		[52]
Episcopaline B (182)		In vivo		[50]
Nagarumine C (176)		In vivo		[46]
Acosinomonine B (178)		In vitro	Inhibition of acetic acid-induced writhing in mice (ED_{50} = 76.0 μ mol/kg) Strong inhibitory effect on the activation of the TRPV1 channel in HEK-293 cells mediated by capsaicin, with an inhibition rate of 31.78% at 10 μ M	[79]
Aconicatisulfonine A (259)		In vivo	Reduction in acetic acid-induced writhing in mice by 43.2%, 64.7%, 63.6%, and 19.3% at 0.3 mg/kg, respectively	[98]
Aconicatisulfonine B (260)		In vivo		[98]
Aconapelsulfonine A (261)		In vivo		[99]
Aconapelsulfonine B (262)		In vivo	Reduction in acetic acid-induced writhing in mice by 31.26%, 26.84%, and 43.8% at 1.0 mg/kg (i.p.)	[99]
Aconicarmisulfonine B (263)		In vivo		[95]
Aconicarmisulfonine C (264)		In vivo		[95]
Aconicarnine E (241)		In vivo	Reduction in acetic acid-induced writhing in mice by 26.35% at 2.0 mg/kg (i.p.)	[93]
Aconidenusulfonine A (288)		In vivo		[104]
Lipojesaconitine (98)	Antitumor	In vitro	Cytotoxicity against A549, MDA-MB-231, MCF-7, and KB with IC_{50} values ranging from 6.0 to 7.3 μ M	[57]
8-O-ethyl-benzoyldeoxyaconine (107)		In vitro	Anticancer activity against A549 (IC_{50} = 12.58 ± 1.82 μ M) and H460 (IC_{50} = 12.76 ± 2.10 μ M) cells	[47]
Brunonianine B (182)		In vitro	Cytotoxicity on Caco-2 (IC_{50} = 3.14 ± 0.37 μ M) and Skov-3 (IC_{50} = 2.20 ± 0.21 μ M) cells and activation of the Bax/Bcl-2/caspase-3 signaling pathway	[80]
Brunonianine C (183)		In vitro	Cytotoxicity on Caco-2 (IC_{50} = 2.41 ± 0.35 μ M) and Skov-3 (IC_{50} = 6.88 ± 0.81 μ M) cells	[80]
Ceylonamide G (281)		In vitro	Cytotoxic to DU145 cells (IC_{50} = 6.9 μ M, MEC = 10 μ M)	[101]
Smirnotine A (94)	Cardioprotective	In vivo	Some preventive effects on aconitine-induced arrhythmia in mice	[58]
Gyalanunine A (253)		In vitro	Significant cardiotonic activity after perfusion in frog hearts and could be related to the β receptor	[89]
Tanguticuline A (199)	Antiviral	In vitro	Inhibition of the cytopathic effect against H1N1 with IC_{50} values of 2.9 and 2.4 μ g/mL, respectively	[85]
Tanguticuline E (203)		In vitro		[85]
Acoapetaludine D (45)	Antibacterial	In vitro	Anti- <i>Helicobacter pylori</i> (MIC = 100 μ g/mL)	[40]
Acoapetaludine E (46)		In vitro	Anti- <i>Helicobacter pylori</i> (MIC = 50 μ g/mL)	[40]
Stylosine A (157)		In vitro	Anti- <i>Staphylococcus aureus</i> (MIC = 2.00 μ g/mL)	[74]

Table 19. Cont.

TeAs Types	Activities	Research Method	Possible Mechanism	Ref.
Stylosine B (158)	Antibacterial	In vitro	Anti- <i>Staphylococcus aureus</i> (MIC = 32.00 µg/mL)	[74]
Koninginol A (284)		In vitro	Anti- <i>Bacillus subtilis</i> (MIC = 10.00 µg/mL)	[102]
Koninginol B (285)		In vitro	Anti- <i>Bacillus subtilis</i> (MIC = 2.00 µg/mL)	[102]
2-O-cinnamoyl hetisine (209)	Antiplasmodial	In vitro	Anti- <i>Plasmodium falciparum</i> strains <i>Pf</i> INDO (IC ₅₀ = 1.92 µM) and the <i>Pf</i> 3D7 (IC ₅₀ = 10.8 µM)	[88]
Apetalrine B (82)	Neuroprotective	In vitro	Neuroprotective activity (77.4%) on H ₂ O ₂ -induced SH-SY5Y cell	[55]
Uncinataine-A (120)	AChEI activity	In vitro	Acetyl-cholinesterase inhibitory activity (IC ₅₀ = 207.73 ± 0.3 µM)	[66]
Anthoroidine G (204)		In vitro	Acetyl-cholinesterase inhibitory activity (IC ₅₀ = 6.3 ± 1.6 µM)	[84]
Anthoroidine I (206)		In vitro	Acetyl-cholinesterase inhibitory activity (IC ₅₀ = 9.3 ± 3 µM)	[84]

Kamaonensines B (**148**) and F (**153**) showed more robust anti-inflammatory activities than the positive drug indomethacin ($9.0 \pm 1.3 \mu\text{M}$), with IC_{50} values of 2.7 ± 0.5 and $0.9 \pm 0.2 \mu\text{M}$, respectively. Network pharmacological studies indicated that the anti-inflammatory mechanism may be related to the MAPK signaling pathway. In addition, molecular docking results showed that the infrequent amides and methylenedioxy groups could be the two critical pharmacophores in **148** and **153** [72].

Aconicumine A (**170**) exhibited anti-inflammatory activity by inhibiting LPS-activated NO production in RAW264.7 cells ($\text{IC}_{50} = 19.7 \pm 1.1 \mu\text{M}$). Structure–activity relationship studies identified the methoxy group at its C-6 position is an effective group for anti-inflammatory activity [77].

Forrestline F (**190**) significantly inhibited NO activity in RAW264.7 cells ($\text{IC}_{50} = 9.57 \pm 1.34 \mu\text{M}$). Further studies showed modulating anti-inflammatory effects through inhibiting ROS production and NF- κ B, MAPK, and Nrf2 signaling pathways [53].

3.2. Analgesic Activity

Opioids and non-steroidal anti-inflammatory drugs (NSAIDs) are the primary drugs for pain treatment [107]. However, both drug classes can cause severe adverse reactions in clinical use. As an essential class of TeAs, the analgesic activity of DAs has been widely studied. Several new compounds with analgesic activity have been reported in the past five years of research. Compounds **89**, **91**, **176**, **180**, **182**, **241**, **259–264**, and **288** showed analgesic activity by inhibiting acetic acid-induced abdominal contractions in mice.

Compounds **89**, **91**, **176**, **180**, and **182** exhibited more excellent analgesic activity than the positive controls aspirin and acetaminophen. Episcopaline B (**182**), Pseudostapine C (**89**), Austroyunnanine B (**91**), and Episcopine A (**180**) significantly reduced acetic acid-induced abdominal contractions in mice in a dose-related manner, with the ID_{50} values of 55.0, 60.3, 48.0, and 66.1 $\mu\text{mol/kg}$, respectively [45,50–52]. Nagarumine C (**176**) demonstrated significant analgesic activity and inhibited acetic acid-induced writhing in mice at 76.0 $\mu\text{mol/kg}$ [46].

Aconicatisulfonines A (**259**) and B (**260**) showed significant analgesic activity against acetic acid-induced writhing in mice, with inhibition rates of 43.2% and 64.7% (morphine, 66.8%) at 0.3 mg/kg, respectively [98]. Aconicarnine E (**241**) inhibited acetic acid-induced writhing in mice by 43.8% at 1.0 mg/kg [93]. Aconapelsulfonines A (**261**) and B (**262**) showed specific analgesic effects at the dose of 0.3 mg/kg, with inhibition rates of 63.6% and 19.3% (morphine, 84.6%), respectively [99]. Aconicarmisulfonines B (**263**) and C (**264**) displayed analgesic effects in mice, with inhibition rates of 31.26% and 26.84%, respectively [95]. Aconidenusulfonine A (**288**) showed analgesic activity, reducing acetic acid-induced writhing in mice by 26.35% at 2.0 mg/kg (i.p.), and its structure–activity relationship indicated that the analgesic activity might be related to a single bond between C-12 and C-16 [104].

The transient receptor vanilloid 1 (TRPV1) channel is a crucial target in developing new analgesics for pain management [108]. Acosinomone B (**178**) showed a strong inhibitory effect on the activation of the TRPV1 channel in HEK-293 cells mediated by capsaicin (0.5 μM), with an inhibition rate of 31.78% at the concentration of 10 μM , making compound **178** a promising analgesic lead structure [79].

3.3. Antitumor Activity

TeAs have proven to be effective chemotherapeutic drugs for various cancers. For example, paclitaxel and its derivatives docetaxel and cabazitaxel have been clinically used for cancer treatment [109]. Over the past five years, studies have identified eight new members of TeAs with potential anticancer activity.

Incarvine G (**12**) showed cytotoxicity with the IC_{50} value of 60.29 μM against MDA-MB-231 cells and inhibited the migration and invasion of breast cancer cells. Further mechanistic studies showed that Incarvine G inhibited the migration and invasion of MDA-MB-231 cells by inhibiting actin cytoskeleton formation [19]. ($\pm$)-Caryopterisines

A (**19**) and B (**20**) reduced kynurenine (Kyn) biosynthesis in HeLa cells by inhibiting indoleamine 2,3-dioxygenase (IDO) at doses of 10 μ M with inhibition ratios of 25.7% and 29.8%, respectively [22]. Given the role of IDO cancer immunotherapy [110], compounds **19** and **20** are highlighted for their potent anticancer activities via IDO inhibition.

Commipholactam A (**27**) showed cytotoxicity against HepG2 and A549 cells, with IC_{50} values of 21.73 ± 2.86 μ M and 128.50 ± 17.06 μ M, respectively [28]. 8-O-ethyl-benzoyldeoxyaconine (**107**) demonstrated strong anticancer activity with an IC_{50} of 12.58 ± 1.82 and 12.76 ± 2.10 μ M against human non-small-cell lung cancer A549 and H460 cells, respectively [47]. Lipojesaconitine (**98**) displayed significant cytotoxicity against four cell lines (A549, MDA-MB-231, MCF-7, and KB) with IC_{50} values ranging from 6.0 to 7.3 μ M. However, it showed weak cytotoxicity against KB-VIN ($IC_{50} = 18.6$ μ M), suggesting potential efflux by P-gp [57].

Brunonianines B (**182**) and C (**183**) showed significant cytotoxicity on Caco-2 (colon cancer) and Skov-3 (human ovarian cancer) cell lines. Compounds **182** and **183** showed comparable cytotoxicity to hydroxycamptothecin (HCPT) against the Caco-2 cell line, with IC_{50} values of 3.14 ± 0.37 and 2.41 ± 0.35 μ M, respectively. Moreover, compound **182** showed stronger cytotoxicity than the HCPT (2.29 μ M) Skov-3 cell line, with an IC_{50} value of 2.20 μ M, likely due to its 19-S conformation. Further mechanistic studies showed that compound **182** could activate the Bax/Bcl-2/caspase-3 signaling pathway to induce apoptosis and effectively inhibit Skov-3 cell proliferation, migration, and invasion [80]. Ceylonamide G (**281**) was cytotoxic to DU145 cells, a human prostate cancer cell line, with an IC_{50} value of 6.9 μ M and a minimum effective concentration (MEC) of 10 μ M [101].

3.4. Cardioprotective Activity

Cardioprotective activity is a unique biological activity of DAs, such as Guan fu base A, which has been clinically developed to treat arrhythmias. Two new DAs with cardioprotective activity have been discovered in the past five years.

Smirnotine A (**94**) has some preventive effects on aconitine-induced arrhythmia in mice. The occurrence of ventricular tachycardia and ventricular flutter was significantly prolonged at 8 mg/kg, and ventricular flutter, ventricular fibrillation, and survival time of mice were prolonged considerably at 16 mg/kg [58]. Gyalanunine A (**253**) showed significant cardiotonic activity after perfusion in frog hearts and significantly inhibited myocardial contraction when combined with β -blockers in isolated frog hearts, suggesting that its mechanism of action may be related to epinephrine β receptors [89]. The existence of a hemiacetal moiety might be the critical structural feature necessary for the cardiac effect of **253** [89].

3.5. Antimicrobial Activity

Natural alkaloids have been proven to possess excellent antimicrobial activity. In the past five years, it has been found that several TeAs exhibit antimicrobial activity, such as antibacterial, antiviral, and antiparasmodial activities.

3.5.1. Antiviral Activity

Forsyqinlingines C-D (**14–15**) and forsyqinlingine A-B (**286–287**) showed antiviral activities against influenza A virus (H1N1) and respiratory syncytial virus (RSV). They exhibited IC_{50} values of 11.9, 15.1, 6.9, and 7.7 μ M, alongside EC_{50} values of 13.5, 14.0, and 5.0 μ M, respectively [21,103]. Tanguticulines A (**199**) and E (**203**) were effective against H1N1, inhibiting the cytopathic effect with IC_{50} values of 2.9 and 2.4 μ g/mL, respectively [85].

3.5.2. Antibacterial Activity

Acoapetaludines D (**45**) and E (**46**) showed weak anti-*Helicobacter pylori* activity with minimum inhibitory concentrations (MICs) of 100 and 50 μ g/mL, respectively [40]. Stylosines A (**157**) and B (**158**) exhibited antibacterial activity against *Staphylococcus aureus* with MIC of 2.00 and 32.00 μ g/mL, respectively [74]. Koninginols A (**284**) and B (**285**) exhibited

significant antibacterial activities (CMCC 63501) with MIC values of 10 and 2 µg/mL, respectively [102].

3.5.3. Antiplasmodial Activity

2-O-cinnamoyl hetisine (**209**) showed antimalarial activity against the *Plasmodium falciparum* strains Pf INDO and Pf 3D7, with the IC₅₀ values of 1.92 µM and 10.8 µM, respectively [88].

3.6. Other Activity

In addition to the widely recognized anti-inflammatory, analgesic, antitumor, and antimicrobial activities mentioned above, recent research reported over the past five years has uncovered several TeAs with other significant biological activities, including vascular relaxation activity, antifibrosis activity, and neuroprotective activities.

Alstochonines A (**1**) and B (**2**) showed moderate vasorelaxant activity with rates of $73.6 \pm 2.8\%$ and $95.4 \pm 3.7\%$, making the first report of the vasorelaxant activity of monoterpene alkaloids [16]. Lomatogonin C(**26**) displayed immunosuppressive activity, further evidenced by the inhibition of T cell proliferation and secretion of its cytokine IFN-γ in T cells stimulated with the anti-CD3/CD28 antibody [26]. (±)-Caryopterisines A (**19**) and B (**20**) inhibited estrogen E2 biosynthesis in human ovarian granulosa-like KGN cells by 57.2% and 39.9% at a dose of 10 µM, respectively.

Caryopterisine C (**16**) showed potential antifibrotic activity without cytotoxicity by inhibiting collagen accumulation (IC₅₀ = 14.26 ± 1.46 µM) in NIH3T3 cells (murine embryo fibroblasts). Further studies into proteins involved in transforming growth factor-β-activated signaling pathways revealed that caryopterisine C (**16**) reduced collagen accumulation by inhibiting ERK1/2, P38, and SMAD2/3 phosphorylation. Apetalrine B (**82**) showed neuroprotective activity, with a neuroprotective rate on H₂O₂-induced SH-SY5Y cell injury of 77.4%. Its neuroprotective effect is believed to be achieved by inhibiting apoptosis [55]. Uncinataine-A (**120**) showed significant acetylcholinesterase (AChE) inhibitory activity, with IC₅₀ values of 207.73 ± 0.3 µM [66]. Anthoroidines G (**204**) and I (**206**) showed certain AChEI activity, with IC₅₀ values of 6.3 ± 1.6 and 9.3 ± 3 µM, respectively [84].

4. Conclusions

This review summarizes the sources, chemical structures, and biological activities of 289 TeAs discovered between 2019 and 2024, including 26 monoterpene alkaloids, 6 sesquiterpene alkaloids, and 257 DAs. DAs are the most abundant class of terpenoid alkaloids widely distributed in *Aconitum* and *Delphinium*. Seven novel DAs (**283–289**) were obtained from *Spongia* sp., *Trichoderma koningii* A729, and *Forsythia suspensa* in the last five years, respectively. Monoterpene alkaloids are mainly distributed in *Apocynaceae*, *Scrophulariaceae*, and *Gentianaceae*, while sesquiterpene alkaloids, the least common class, are found in *Dendrobium*.

The majority of TeAs exhibit anti-inflammatory, antitumor, and antimicrobial properties. Among the terpenoid alkaloids discovered in the past five years, the analgesic activity is unique to diterpene alkaloids. Distinctively, the analgesic activity has been identified exclusively in diterpene alkaloids, with several DAs demonstrating analgesic effects in mice superior to standard drugs like aspirin and acetaminophen, including Episcopaline B, Pseudostapine C, and Austroyunnanine B. These findings support the potential for developing novel analgesics. Moreover, TeAs show promise as therapeutic agents for various cancers, exhibiting inhibitory effects on breast, intestinal, liver, lung, and cervical cancer cells in vitro. The efficacy of these compounds in vivo remains an area for future research. TeAs also hold potential as cardiovascular medications, exemplified by compounds like Smirnotine A, which has shown heart-protective activity.

While current research has revealed a broad spectrum of TeAs' biological activities, most of these studies have been limited to in vitro cell viability assessments. There is a significant need for further in vivo pharmacological studies to understand the therapeutic

potential of TeAs against various diseases comprehensively. This review has compiled the sources, structural characteristics, and biological activities of newly discovered compounds within the last five years, aiming to serve as a valuable resource for the continued exploration and application of terpenoid alkaloids in therapeutic contexts.

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Abbreviations

TeAs	Terpenoid alkaloids
MEP	Methylerythritol phosphate
NMR	Nuclear magnetic resonance
HR-ESI	High-resolution mass spectrometry
ECD	Electron capture detector
DAs	Diterpenoid alkaloids
TNF- α	Tumor necrosis factor- α
IL-1 β	Interleukin-1 β
NF- κ B	Nuclear factor- κ B
TRPV1	Transient receptor vanilloid 1
MEC	Minimum effective concentration
HEK-293	Human Embryonic Kidney 293 Cells
LPS	Lipopolysaccharide
COX-2	Cyclooxygenase-2
PMNs	Polymorphonuclear leukocytes
PAF	Platelet-activating factor
MAPK	Mitogen-activated protein kinase
AChE	Acetylcholinesterase
MICs	Minimum inhibitory concentrations
IC ₅₀	Half maximal inhibitory concentration
ID ₅₀	Half infectious dose
ERK1/2	Extracellular signal-regulated kinase 1/2
ROS	Reactive oxygen species
Nrf2	NF-E2-related factor 2
Kyn	Kynurenine
IDO	Indoleamine 2,3-dioxygenase
P-gp	P-glycoprotein
HCPT	Hydroxy camptothecin
RSV	Respiratory syncytial virus
H1N1	Influenza A virus
IFN- γ	Interferon- γ
Bax	Bcl-2-associated X protein
Bcl-2	B-cell lymphoma-2

P38	p38 mitogen-activated protein kinase (MAPK)
SMAD 2/3	Mothers against decapentaplegic homolog 2/3
CMCC 63501	<i>Bacillus subtilis</i>
Me	Methyl
Et	Ethyl
Ibut	Isobutyryl
Mb	2-methylbutyryl
Bz	Benzoyl
As	Anisoyl
Vr	Veratroyl
Cinn	Cinnamoyl
Ant	Anthranoyl
Glc	Glucose
Ac	Acetyl
pHb	p-hydroxybenzoyl
lipo	Stearoyl,oleoyl,linolenoyl,linoleoyl,palmitoyl

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