

# 中国乌头属植物药用亲缘学研究

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## A pharmacophylogenetic study of *Aconitum* L. (Ranunculaceae) from China

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**Abstract** *Aconitum* L. (Ranunculaceae) is a large genus of about 300 species distributed in the temperate regions of the Northern Hemisphere. This genus consist of three well-circumscribed subgenera, subgen. *Lycocotonum* (DC.) Peterm., subgen. *Aconitum* and subgen. *Gymnaconitum* (Stapf) Rapács. The southwestern China, particularly its Hengduan Mountains region, is the most important center of diversity and speciation of the genus. Many species in this genus have been used as poisonous and medicinal plants. This paper is to evaluate the taxonomic value of diterpenoid alkaloids mainly at subgeneric and serial levels of the genus *Aconitum* based on an analysis of the distribution of diterpenoid alkaloids in the Chinese species and of their biogenetic pathways. The correlation between phylogeny, chemical constituents and pharmaceutical uses in the genus *Aconitum* is also discussed from the data of the toxicity and therapeutic value of the species in the genus, a research field for which the term “pharmacophylogenetics” is here specifically coined. The major points of the paper are summarized as follows:

1. Diterpenoid alkaloids known in plants fall into four skeletal types: C<sub>18</sub>, C<sub>19</sub>, C<sub>20</sub> and bisditerpenoid alkaloids. They can be further subdivided into 14 subgroups, namely, C<sub>18</sub>: appaconine-type (I) and ranaconine-type (II); C<sub>19</sub>: aconitine-type (III), lycocotonine-type (IV), 7,17-seco-type (V) and lactone-type (VI); C<sub>20</sub>: atisine-type (VII), denudatine-type (VIII), hetidine-type (IX), hetisine-type (X), veatihine-type (XI) (not found in *Aconitum* species), napelline-type (XII) and anopterine-type (XIII) (not found in *Aconitum* species); and bisditerpenoid alkaloids (XIV).

2. The species in *Aconitum* subgen. *Lycocotonum* contain mainly the C<sub>18</sub>-diterpenoid alkaloids (lappaconine-type and ranaconine-type) and C<sub>19</sub>-diterpenoid alkaloids (lycocotonine-type). Roots of the plants in this subgenus show a relatively lower toxicity (LD<sub>50</sub> to mice=1660–3340 mg/kg (i.v.)) and have been used for the treatment of rheumatism, pains and irregular menstruation etc. Because of the lower toxicity of the roots, the species in this

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subgenus are worthy a more detailed phytochemical investigation for the development of new medicines.

3. *Aconitum* subgen. *Aconitum* is the largest subgenus, with about 250 species which are usually divided into two sections, section *Sinaconitum*, a monotypic section including only *A. polycarpum*, and section *Aconitum* including the remaining species. The species in China in the latter section are usually divided into nine series. (1). Series *Tangutica* and series *Rotundifolia* are all dwarf alpine plants, generally less than 35 cm tall. Phytochemically, they contain mainly the lactone-type C<sub>19</sub>-diterpenoid alkaloids and sporadically C<sub>20</sub>-diterpenoid alkaloids. The lactone-type alkaloids have been found so far to occur exclusively within these two series, and thus can be considered as the characteristic chemical constituents of these two series. The roots in the plants of the two series show a relatively lower toxicity (LD<sub>50</sub> to mice = ca. 2400 mg/kg (i.v.)). The whole plants of the species have been traditionally used in China's Tibetan, Mongolian and Uygur regions for the treatment of high fever. (2). The species in series *Bullatifolia* contain mainly the denudatine-type and the napelline-type C<sub>20</sub>-diterpenoid alkaloids, and the aconitine-type C<sub>19</sub>-diterpenoid alkaloids. This series may occupy a somewhat intermediate position in *Aconitum* subgen. *Aconitum* from a chemotaxonomic view. In toxicity, the LD<sub>50</sub> to mice range from 210–270 mg/kg (i.v.). The roots in this series have been used for the treatment of pains and rheumatism. (3). Series *Brachypoda* includes *A. brachypodium*, *A. pendulum*, *A. polyschistum* and several other morphologically very similar species. Their roots are recorded as "Xue-shang-yi-zhi-hao" in the Chinese *Materia Medica* and have been used as anti-rheumatic and analgesic remedies. Phytochemically, they contain mainly the aconitine-type C<sub>19</sub>-diterpenoid alkaloids, an evolutionarily advanced type. The LD<sub>50</sub> to mice range from 130–280 mg/kg (i.v.). It is noteworthy that *A. coreanum* contains mainly the C<sub>20</sub>-diterpenoid alkaloids and has a much lower toxicity (LD<sub>50</sub> = 2800 mg/kg (i.v.) to mice) than the other species in this series. From a chemotaxonomic view it seems reasonable to segregate *A. coreanum* and its closest ally, *A. anthoroideum*, from series *Brachyloda* to establish an independent series. (4). Series *Stylosa*, with plants generally of larger roots, are the major sources of "Da-wu-tou". The species in the series contain mainly the aconitine-type diester C<sub>19</sub>-diterpenoid alkaloids, which are characterized by the presence of anisoyloxy residues at C-14. The roots display a high toxicity with the LD<sub>50</sub> to mice ranging from 24–102 mg/kg (i.v.). From a chemotaxonomic view, *A. contortum*, mainly with the presence of the hetidine-type C<sub>20</sub>-diterpenoid alkaloids and the dranaconine-type C<sub>18</sub>-diterpenoid alkaloids and yet the absence of anisoyloxy residues, seems to be a very special species in series *Stylosa*. Its systematic position needs to be reconsidered. (5) Series *Ambigua*, eight species of which have been investigated phytochemically, contains mainly the aconitine-type C<sub>19</sub>-diterpenoid alkaloids with anisoyloxy residues, indicating its close affinity to series *Stylosa*. (6). Series *Volubilia*, which is characterized by having twining stems, contains the aconitine-type diester C<sub>19</sub>-diterpenoid alkaloids with the presence of an anisoyl or a benzoyl group at C-14. Several species in this series, such as *A. szukinii* and *A. volubile*, contain the highly advanced 15-hydroxyl aconitine-type C<sub>19</sub>-diterpenoid alkaloids, indicating its possible affinity to series *Inflata*. The LD<sub>50</sub> to mice range from 84–283 mg/kg (i.v.). The roots of many species in this series have been used as folklore drugs for the treatment of trauma and rheumatic pains. In this series, *A. hemsleyanum*, a very polymorphic species in gross-morphology, exhibits also a great

interpopulational phytochemical variation. (7). Series *Inflata* includes the two most widely medicinally used *Aconitum* species, *A. carmichaeli* and *A. kusnezoffii*. Both are now officially listed in the Chinese pharmacopoeia. They contain the aconitine-type 15-hydroxyl monoester or diester C<sub>19</sub>-diterpenoid alkaloids, highly advanced chemical constituents in the genus *Aconitum*. The LD<sub>50</sub> to mice range from 66–137 mg/kg (i.v.). The cardiovascular, muscle-smoothing and central effects of the two species have been thoroughly studied. (8). Series *Grandituberosa*, which is morphologically characterized by having several chain-like arranged tubers, contains the highly advanced aconitine-type C<sub>19</sub>-diterpenoid alkaloids. The roots, with the LD<sub>50</sub> to mice being 29 mg/kg (i.v.), have a high toxicity. (9). Series *Racemulosa*, with only *A. racemulosum* var. *pengzhouense* phytochemically already studied in detail and from it a novel skeleton of C<sub>20</sub>-diterpenoid alkaloids, i.e. racemulosine, being found, shows extraordinary chemical features. It contains mainly, however, the lycocotonine-type and the aconitine-type amino alcohol C<sub>19</sub>-diterpenoid and C<sub>20</sub>-diterpenoid alkaloids. The roots of *A. racemulosum* are known as “Xue-Wu” and have the actions of activating blood circulation and removing stasis. From a chemotaxonomic view, this series show some primitive features. (10). Series *Brunnea* is phytochemically not well known. This series contains both C<sub>20</sub>-diterpenoid alkaloids, e.g. denudatine and songorine, and the highly advanced aconitine-type alkaloids, indicating its intermediate position between the series *Bullatifolia* and the series *Brachypoda*.

4. The monotypic subgenus *Gymnaconitum*, with only *A. gymnantrum*, is of both primitive and advanced features phytochemically and gross-morphologically. The whole plant of this species is used as insecticide.

In summary, 76 *Aconitum* species in China have been medicinally used. They are mainly used for the treatment of plaque, sepsis, intoxication, cold- and immuno-suppression-induced ailments, rheumatoid arthritis, and various types of pain, including migraine, swelling induced by trauma and fracture, and facial paralysis. Pharmacologically, they can be developed as analgesic, antirheumatic and anti-arrhythmic agents. The key obstacle for their extensive medical utilization may lie in their usually extremely high toxicity. From a pharmacophylogenetic point of view, therefore, the less toxic species, i.e. those in subgenus *Lycocotonum*, and in series *Tangutica*, *Rotundifolia* and *Racemulosa*, and two species (*A. coreanum* and *A. anthoroideum*) in series *Brachypoda* in subgenus *Aconitum*, should be paid much more attention. Further comprehensive studies on these species are needed for their better medical utilization.

**Key words** *Aconitum* L., chemotaxonomy, ethnopharmacology, pharmacophylogenetics, Ranunculaceae.

**摘要** 毛茛科Ranunculaceae乌头属*Aconitum* L.植物作为有毒植物及药用植物一直受到广泛的关注。本属全世界约有300余种, 其中超过半数分布在中国。本文在总结乌头属二萜生物碱的化学分类及其分布、特征性二萜生物碱及其分类价值以及二萜生物碱的生源关系及其分类学意义的基础上, 结合其毒性和疗效讨论了国产乌头属植物亲缘关系、化学成分和疗效及毒性之间的相关性, 亦即药用亲缘学的初步研究。发现牛扁亚属subgen. *Lycocotonum*是以牛扁碱和C<sub>18</sub>-二萜生物碱为主的类群, 由于其毒性中等, 因而是寻找镇痛、抗炎等新药的一个对象。从二萜生物碱化学成分来看, 露蕊乌头亚属subgen. *Gymnaconitum*并不显得最为进化, 对其分类位置尚难作出最后的结论。乌头亚属subgen. *Aconitum*亚属下系之间的化学分类表现出如下特征: (1)唐古特乌头系ser. *Tangutica*和圆叶乌头系ser. *Rotundifolia*是以内酯型二萜生物碱为主的类群, 毒性较小, 是新药寻找的重点研究类群。保山乌头系ser. *Bullatifolia*以C<sub>20</sub>-二萜生物碱

如光翠雀碱和宋果灵以及C<sub>19</sub>-二萜生物碱如乌头碱、滇乌碱和尼奥灵等为主。短柄乌头系ser. *Brachypoda*显示以3-乙酰乌头碱、乌头碱、伏乌碱等高度进化的乌头碱型二萜生物碱为主，胺醇类如尼奥灵次之，有时共存其他纳哌啉型C<sub>20</sub>-二萜生物碱的特征。准噶尔乌头系ser. *Grandituberosa*的化学特征是以高度进化的乌头碱型如乌头碱等和比较原始的胺醇如塔拉萨敏、尼奥灵等以及C<sub>20</sub>-二萜生物碱为主，均有较大毒性。褐紫乌头系ser. *Brunnea*则以C<sub>20</sub>-二萜生物碱如光翠雀碱和宋果灵为主，杂有高度进化的乌头碱型二萜生物碱如乌头碱等成分。化学分类上不支持其独立成为一个分支。以上各系组成乌头亚属的原始和中间过渡类群。其中唐古特乌头系和圆叶乌头系最为相近，褐紫乌头系可能是连接保山乌头系和短柄乌头系的“桥梁”，而准噶尔乌头系更靠近保山乌头系。(2)显柱乌头系ser. *Stylosa*是以含大茴香酸酯基的乌头碱型二萜生物碱以及塔拉萨敏和查斯曼宁胺醇类为主的类群，是块根较大的“大乌头”的主要来源，具有很大的毒性。兴安乌头系ser. *Ambigua*以含大茴香酸酯基的乌头碱型和原始胺醇类如塔拉萨敏、尼奥灵等二萜生物碱为主。蔓乌头系ser. *Volvilia*是以含大茴香酸酯基/苯甲酸酯基的乌头碱型和塔拉萨敏胺醇类以及高度进化的乌头碱型二萜生物碱为主的中间过渡类群。乌头系ser. *Inflata*以含15-羟基的单酯、双酯或多酯以及胺醇类乌头碱型二萜生物碱为主，且酯基中无大茴香酸酯基，此系是草乌的主要植物来源，具有很大的毒性，应十分慎用。这些系可能代表乌头亚属进化的类群。其中显柱乌头系与兴安乌头系可能较近缘。蔓乌头系可能是连接显柱乌头系/兴安乌头系与乌头系的中间类群。另外，保山乌头系、短柄乌头系和准噶尔乌头系可能是直接向显柱乌头系、蔓乌头系和乌头系过渡的较为原始的类群。(3)岩乌头系ser. *Racemulosa*从化学分类角度来看是一个特殊的类群，支持其独立成一个分支。其化学特征以牛扁碱型和乌头碱型的胺醇二萜生物碱如牛扁碱、异塔拉萨亭定和C<sub>20</sub>-二萜生物碱为主。如果单纯从化学成分来看，它与牛扁亚属植物似乎有一定关系。

**关键词** 乌头属；化学分类；传统药物学；毛茛科；药用亲缘学

毛茛科Ranunculaceae乌头属*Aconitum* L.全世界约有300余种，广泛分布于北半球温带地区，主要分布于亚洲，其次是欧洲和北美洲。我国已记录200多种(Li & Kadota, 2001)。我国西南横断山区南部(四川西部、云南西北部和西藏东部)是国产乌头属植物的重要分布区。

由于乌头属植物是重要的有毒植物，并具有药用价值，因此一直受到广泛的关注。但乌头属是一个分类上十分困难的类群，其形态变异极为复杂。为此，许多分类学家对乌头属植物的分类作了相当多的研究(罗艳, 杨亲二, 2005)。王文采(1979)对国产乌头属进行了属下系统的划分。Tamura(1995)对全世界的乌头属植物进行了系统整理。可是，两位学者对亚属下的组的观点却相差较远(罗艳, 2003)，其原因是各人所依据的分类性状不同。日本学者Kadota(2001)又将甘青乌头系ser. *Tangutica* W. T. Wang升级为亚属subgen. *Tangutica* (W. T. Wang) Kadota，从而使乌头属包括4个亚属，即牛扁亚属subgen. *Lycocotonum* (DC.) Peterm.、乌头亚属subgen. *Aconitum*、露蕊乌头亚属subgen. *Gymnaconitum* (Stapf) Rapalcs和subgen. *Tangutica* (W. T. Wang) Kadota。分子系统学(罗艳, 2003; Luo et al., 2005)不支持这种划分。近年来，杨亲二等(Yang et al., 1989; 杨亲二, 1990, 1999, 2001；杨亲二等, 1993a, b, 1994；罗艳, 2003; Luo et al., 2005)围绕着国产乌头属植物的分类和系统演化，从形态学、细胞学和分子系统学等方面进行了研究，提出了若干新的观点。

二萜生物碱是一类结构复杂而又颇具分类价值的特征性化合物。迄今，报告的天然产二萜生物碱已逾900个，其中80%以上分自毛茛科乌头属、翠雀属*Delphinium* L.和飞燕草属*Consolida* (DC.) S. F. Gray植物中。初步统计，目前已从国产84种乌头属植物中分出

421种二萜生物碱(表2—4)。

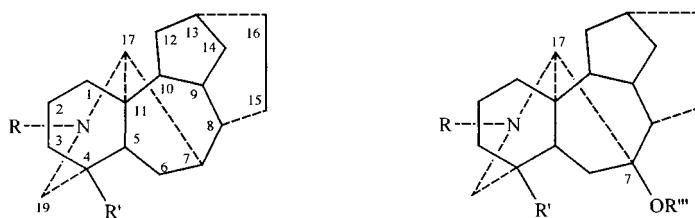
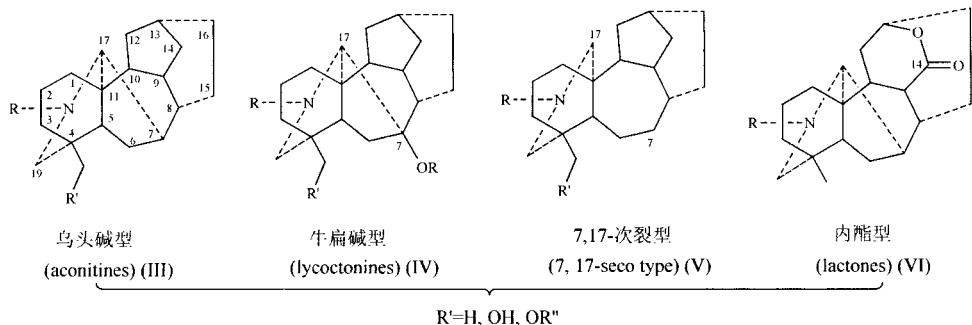
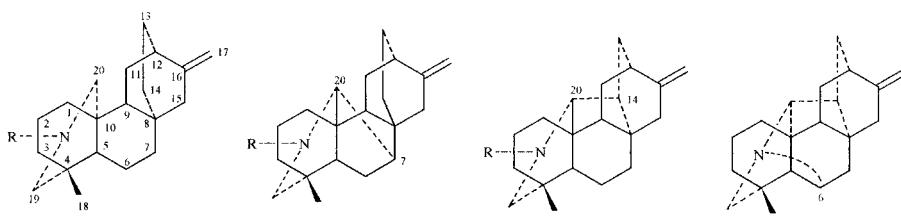
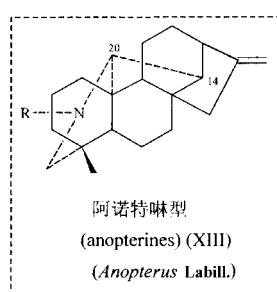
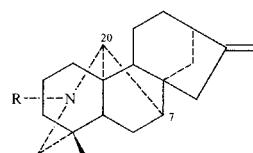
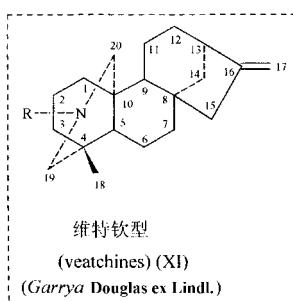
Ichinohe(1978)开拓性地提出了二萜生物碱的生源关系的假设,认为这种关系反映了乌头属、翠雀属和飞燕草属之间的系统演化关系。应指出的是Ichinohe的许多观点已被后来大量的研究事实所证明。近年来,他又报告了乌头属植物化学分类的新研究结果(Ichinohe, 2002; Ichinohe et al., 2002)。肖培根等(1983)最先对国产27种乌头属植物的根部形态与亲缘、成分和毒性的关系作了研究,指出了滇乌碱类生物碱在乌头属植物化学分类上的价值(肖培根等, 1983)以及露蕊乌头*Aconitum gymnanthrum* Maxim.的植物化学研究结果不表明该种是高度进化的类群(肖培根, 1984)。郝小江等(1985)在上述研究的基础上,系统探讨了二萜生物碱在国产乌头属植物中的分布与该属的属下系统和地理分布的相关性。20年来,国产乌头属植物的化学、分类和系统演化以及药用等方面的研究取得了不少进展,使我们有可能对国产乌头属植物亲缘关系、化学成分和疗效间的相关性,即药用亲缘学方面进行一次初步的探索,为探讨该属植物的分类、系统演化提供更多植物化学的证据,同时也为本属植物的进一步开发利用提供线索。

## 1 二萜生物碱的分类及其分布

### 1.1 分类

二萜生物碱分类的原则和类型随着研究的不断深入而变化。Pelletier和Mody(1979, 1981)将二萜生物碱分为两大类: C<sub>19</sub>-和C<sub>20</sub>-二萜生物碱类。再按骨架将C<sub>19</sub>和C<sub>20</sub>类分别分为: 乌头碱(aconitines)型、牛扁碱(lycoctonines)型、内酯(lactones)型以及维特钦(veatchines)型、阿替生(atisines)型和双二萜生物碱(bisditerpenoids)型。王锋鹏和方起程(1983)从C<sub>19</sub>-二萜生物碱中划分出C<sub>18</sub>-二萜生物碱,并采用多数学者意见将C<sub>20</sub>-二萜生物碱细分为阿替生型、光翠雀碱(denudatines)型、海替定(hytidines)型、海替生(hytisines)型、维特钦型、纳哌琳(napellines)型、阿诺特琳(anopterines)型和德尔鲁定(delnudines)型(Wang & Liang, 1992)。Sultankhodzhaev和Nishanova(1995)将二萜生物碱分成四大类: 阿替烷类(C<sub>20</sub>)、考烷类(C<sub>20</sub>)、乌头烷类(C<sub>18</sub>/C<sub>19</sub>)和双二萜生物碱类(C<sub>20</sub> × 2)。该分类的缺点是大类下划分含混。Wang和Liang(2002)又从C<sub>19</sub>-二萜生物碱中再划分出7,17-次裂型和重排型以及化学上将C<sub>20</sub>-二萜生物碱分为4大类20类型35亚型43组。Ichinohe(1978, 2002)和Ichinohe等(2002)则从植物化学分类角度将二萜生物碱分成11类,并将7,17-次裂型分称为原乌头宁碱型(protoaconines)和原牛扁碱型(protolycoctonines)以及将C<sub>18</sub>类分为高乌宁碱型(lappaconines)和冉乌宁碱型(ranaconines),我们同意这种划分。

综上所述,这里从植物化学分类的角度,将二萜生物碱分为四大类(C<sub>18</sub>、C<sub>19</sub>、C<sub>20</sub>和双二萜)14类型(图1)。

(1) C<sub>18</sub>-二萜生物碱类(C<sub>18</sub>-diterpenoid alkaloids)高乌宁碱型  
(lappaconines) (I)冉乌宁碱型  
(ranaconines) (II) $R'=H, OH, OR''$      $R'''=H, OH$ (2) C<sub>19</sub>-二萜生物碱类(C<sub>19</sub>-diterpenoid alkaloids)鸟头碱型  
(aconitines) (III)牛扁碱型  
(lycoctonines) (IV)7,17-次裂型  
(7, 17-seco type) (V)内酯型  
(lactones) (VI) $R'=H, OH, OR''$ (3) C<sub>20</sub>-二萜生物碱类(C<sub>20</sub>-diterpenoid alkaloids)阿替生型  
(atisines) (VII)光翠雀碱型  
(denudatines) (VIII)海替定型  
(hetidines) (IX)海替生型  
(hetisines) (X)

## (4) 双二萜生物碱类(bisditerpenoid alkaloids)

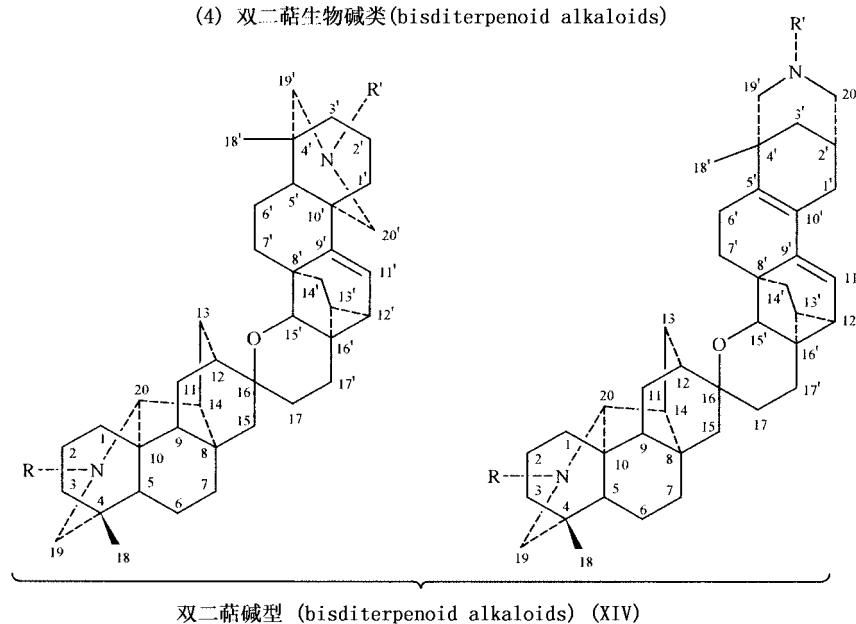


图1 根据植物化学分类进行的二萜生物碱分类

Fig. 1. The skeletal types of diterpenoid alkaloids with reference to chemotaxonomy.

应指出的是, 用来区别乌头碱型(III)、高乌宁碱型(I)和牛扁碱型(IV)、冉乌宁碱型(II)的许多结构特征, 如C-1和C-6取代基构型等, 由于分离鉴定的化合物数量不断增加而不再成立。直到现在, 二者结构上的唯一区别仅是C-7氧取代基的有无。

## 1.2 分布

截止2002年底, 从植物中分出的二萜生物碱逾900个, 它们分属于5科8属植物中(表1)。

由表1看出, C<sub>18</sub>-二萜生物碱主要分布于乌头属, 在翠雀属中仅零星存在。C<sub>19</sub>-二萜生物碱主要分布于乌头属、翠雀属和飞燕草属。C<sub>20</sub>-二萜生物碱则分布于全部8个属中。其主要分布类群为乌头属、翠雀属、飞燕草属, 其次为绣线菊属*Spiraea* L., 再次为*Garrya* Douglas ex Lindl. 属和*Anopterus* Labill. 属。在酸模属*Rumex* L. 仅一种植物*R. pictus* Forssk. 含有3个二萜生物碱化合物(Wang & Liang, 2002)。又由于维特钦型(XI)和阿诺特啉型(XIII)至今未在毛茛科植物中发现, 故不在本文讨论范围之内(图1中虚线示出)。而就二萜生物碱类型分布来说, 除维特钦型(XI)、阿诺特啉型(XIII) 和双二萜生物碱型(XIV)外, 其余类型都分布于乌头属。翠雀属则主要分布有牛扁碱型(IV)以及乌头碱型(III)和海替生型(X)。应强调的是, 双二萜生物碱型(XIV)也主要存在于翠雀属植物(*D. staphisagria* L.)中。

为便于对国产乌头属植物的亲缘关系和化学成分之间的相关性进行归纳分析, 本文根据王文采(1979)的分类系统, 汇列出该属植物中二萜生物碱的分布(表2-4)。

表1 二萜生物碱在植物中的分布

Table 1 Distribution of diterpenoid alkaloids in plants

分类群 Taxon	二萜生物碱 Diterpenoid alkaloid		
	C <sub>18</sub>	C <sub>19</sub>	C <sub>20</sub>
1. 毛茛科Ranunculaceae			
1) 乌头属 <i>Aconitum</i> L.	I, II	III, IV, V, VI	VII, VIII, IX, X, XI, XII
2) 翠雀属 <i>Delphinium</i> L.*	...	III**, IV	X, XIV
3) 飞燕草属 <i>Consolida</i> (DC.) S. F. Gray	-	IV	VIII, X
4) 唐松草属 <i>Thalictrum</i> L.	-	-	VII, IX
2. 蔷薇科Rosaceae			
5) 绣线菊属 <i>Spiraea</i> L.	-	-	VII, IX, X
3. Garryaceae			
6) <i>Garrya</i> Douglas ex Lindl.	-	-	XI
4. Escalloniaceae			
7) <i>Anopterus</i> Labill.	-	-	XIII
5. 莠科Polygonaceae			
8) 酸模属 <i>Rumex</i> L.	-	-	X

“-”示零分布，“...”示少数散在分布。\*与乌头属比较，有阿替生型、光翠雀碱型、海替定型、海替生型分布的种类很少；\*\*乌头碱型分布很少(约11种)。

“-”no distribution, “...” sporadic distribution; \* in comparison with *Aconitum* only a few species in this genus have atisines, denudatines, hetidines and hetisines; \*\* aconitines present only in ca. 11 species.

## 2 特征性二萜生物碱及其分类学价值

植物化学分类的关键是选取和处理特征性化学成分，以及参考其他分类(形态、细胞、分子系统学等)研究的同时，考察同一类群中不同特征性化学成分的分布情况。显然，二萜生物碱就是乌头属、翠雀属和飞燕草属植物分类的重要的特征性成分。这里，我们将逐一讨论这些特征性化学成分及其分类学价值。

### 2.1 结构类型

如表1所示，二萜生物碱的结构类型在属的区分上显示出明显的特征性。C<sub>20</sub>-二萜生物碱绝大多数类型分布于乌头属，其中纳哌啉型则几乎全部存在于该属中。从翠雀属植物分离得到的C<sub>20</sub>-二萜生物碱却很少。这些特征均具有比较重要的分类学意义。但是，与C<sub>20</sub>-二萜生物碱比较，C<sub>18</sub>-和C<sub>19</sub>-二萜生物碱则更具有分类价值。C<sub>20</sub>-二萜生物碱的原始性则更多地体现在生源上前体物的地位。一般地，骨架环系复杂程度愈高则愈进化。所以，C<sub>19</sub>-二萜生物碱要比C<sub>20</sub>-二萜生物碱更进化些。在C<sub>20</sub>-二萜生物碱中，其复杂程度按照阿替生型<光翠雀碱型<纳哌啉型、海替定型<海替生型顺序变化。C<sub>18</sub>-二萜生物碱可视由C<sub>19</sub>-二萜生物碱降解而来，故似应更进化些，但其分布却处于相对更原始的牛扁亚属植物中。对于该属中C<sub>19</sub>-二萜生物碱来说，可认为C<sub>18</sub>-二萜生物碱是原始中的进化。所以，C<sub>18</sub>-二萜生物碱所具有的分类价值仍不容忽视。

迄今从乌头属植物中仅分得3个内酯型二萜生物碱，且全部分布于乌头亚属比较原始的类群如甘青乌头系等类群中。其结构和存在的原始性达到高度的一致性。所以，内酯型二萜生物碱对亚属下系的划分应具有相当重要的参考价值。

表2 中国乌头属牛扁亚属植物中二萜生物碱成分

Table 2 Diterpenoid alkaloids in *Aconitum* subgenus *Lycocotonum* (DC.) Peterm. from China

	分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
1 黄毛乌头		C <sub>19</sub> .(1) chasmanine	A	Pelletier et al. (1984)
	<i>A. chrysotrichum</i> W. T. Wang			
2 短距乌头		C <sub>19</sub> .(8) acobretine A	A	Rahman & Choudhary (1995)
	<i>A. brevicalcaratum</i> (Finet & Gagnep.) Diels	acobretine B	A	Rahman & Choudhary (1995)
		acobretine C	A	Rahman & Choudhary (1995)
		acobretine D	A	Rahman & Choudhary (1995)
		acobretine E	A	Rahman & Choudhary (1995)
		scaconine	A	Rahman & Choudhary (1995)
		scaconitine	A	Rahman & Choudhary (1995)
		N-deacetylscaconitine	A	Rahman & Choudhary (1995)
3 花萼乌头*		C <sub>19</sub> .(3) N-deacetylscaconitine	A	Pelletier & Joshi (1991)
	<i>A. scaposum</i> Franch.*	scaconine	A	Pelletier & Joshi (1991)
		scaconitine	A	Pelletier & Joshi (1991)
3a 聚叶花萼乌头*		C <sub>19</sub> .(6) N-deacetylscaconitine	A	Yunusov (1991)
	<i>A. scaposum</i> var. <i>vaginatum</i> (Pritz.) Rapaics*	scaconine	A	Yunusov (1991)
		scaconitine	A	Yunusov (1991)
		vaginadine	B	Yunusov (1991)
		vaginaline	B	Yunusov (1991)
		vaginatine	B	Yunusov (1991)
4 赣皖乌头*		C <sub>18</sub> .(9) N-deacetylfinaconitine	D	Pelletier et al.(1984)
	<i>A. finetianum</i> Hand.-Mazz.*	N-deacetyl lappaconitine	C	Pelletier et al.(1984)
		N-deacetyl ranaconitine	D	Pelletier et al.(1984)
		finaconitine	D	Pelletier et al.(1984)
		lappaconitine	C	Pelletier et al.(1984)
		ranaconitine	D	Pelletier et al.(1984)
		9-deoxylappaconitine	C	Yunusov (1991)
		isolappaconitine	D	Yunusov (1991)
		neofinaconitine	C	Yunusov (1991)
		C <sub>19</sub> .(7) finetiadine	B	Rahman & Choudhary (1999)
		avadharidine	B	Pelletier et al. (1984)
		delcosine	B	Pelletier et al. (1984)
		lycoctonine	B	Pelletier et al. (1984)
		ajacine	B	Yunusov (1991)
		anthranoylllycoctonine	B	Yunusov (1991)
		delsoline	B	Pelletier et al. (1984)
5 两色乌头*		C <sub>20</sub> .(1) finetianine	BI	Rahman & Choudhary (1995)
	<i>A. alboviolaceum</i> Kom.*	C <sub>19</sub> .(11) ajacine	B	Yunusov (1993)
		avadharidine	B	Yunusov (1993)
		lycoctonine	B	Yunusov (1993)
		lycaconitine	B	Yunusov (1993)
		alboviolaconitine A	B	Rahman & Choudhary (1999)
		alboviolaconitine B	B	Rahman & Choudhary (1999)
		alboviolaconitine C	B	Rahman & Choudhary (1999)
		alboviolaconitine D	B	Rahman & Choudhary (1999)
		septentriodine	B	Rahman & Choudhary (1999)
		avadharidine	B	Rahman & Choudhary (1999)

表2(续) Table 2 (continued)

	分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
6 高乌头*	<i>A. sinomontanum</i> Nakai*	puberaconitine	B	Rahman & Choudhary (1999)
		C <sub>20</sub> : (1) albovionitine	AIII	Rahman & Choudhary (1995)
		C <sub>18</sub> : (13) N-deacetylappaconitine	C	Peng et al. (2000c)
		lappaconine	C	Peng et al. (2000c)
		lappaconidine	C	Peng et al. (2000c)
		N-deacetylranaconitine	D	Peng et al. (2000c)
		8-O-acetyllexcelsine	C	Peng et al. (2000c)
		excelsine	C	Peng et al. (2000c)
		lappaconitine	C	Pelletier et al. (1984)
		ranaconitine	D	Pelletier et al. (1984)
6a 狹盔高乌头*	<i>A. sinomontanum</i> var. <i>angustius</i> W. T. Wang*	sinomontanine C	A	unpublished data
		sinomontanine A	A	unpublished data
		sinomontanine B	A	unpublished data
		sinomontanine D	D	Peng et al. (2000e)
		sinomontanine E	C	Peng et al. (2000e)
		C <sub>19</sub> : (2) sinomontantine A	A	Wang & Sheng (2001)
		sinomontantine B	A	Wang & Sheng (2001)
		C <sub>20</sub> : (1) septatisine	AIII	Rahman & Choudhary (1995)
		C <sub>18</sub> : (3) ranaconitine	D	Rahman & Choudhary (1995)
		lappaconitine	C	Rahman & Choudhary (1995)
7 白喉乌头*	<i>A. leucostomum</i> Worosch.*	3-acetylaconitine	A	Rahman & Choudhary (1995)
		C <sub>18</sub> : (9) leucostine	B	Rahman & Choudhary (1999)
		leuconime	D	Rahman & Choudhary (1999)
		N-deacetylappaconitine	C	Rahman & Choudhary (1999)
		hydroxylappaconine	C	Pelletier et al. (1984)
		lappaconidine	C	Pelletier et al. (1984)
		lappaconine	C	Pelletier et al. (1984)
		lappaconitine	C	Rahman & Choudhary (1999)
		N-acetylsepaconitine	C	Yunusov (1991)
		sepaconitine	C	Yunusov (1991)
8 紫花高乌头	<i>A. septentrionale</i> Koelle	C <sub>19</sub> : (8) leucostine A	B	Rahman & Choudhary (1999)
		leucostine B	B	Rahman & Choudhary (1999)
		delsoline	B	Rahman & Choudhary (1999)
		delcosine	B	Rahman & Choudhary (1999)
		6,14-dimethoxyforesticine	A	Rahman & Choudhary (1999)
		anthranoylllycoctonine	B	Rahman & Choudhary (1999)
		puberaconitine ethylester	B	Yunusov (1993)
		C <sub>20</sub> : (4) 11-acetyllepenine	AII	Rahman & Choudhary (1995)
		acsinatine	AIV	Rahman & Choudhary (1995)
		songorine	BI	Wang & Liang (2002)
8 紫花高乌头	<i>A. septentrionale</i> Koelle	lepenine	AII	Wang & Liang (2002)
		C <sub>18</sub> : (17) acoseptrine	D	Rahman & Choudhary (1995)
		acosepticine	D	Rahman & Choudhary (1995)
		4-anthranoyletapaconidine	A	Rahman & Choudhary (1995)
		leuconime	D	Usmanova et al. (1999)
		ranaconitine	D	Pelletier et al. (1984)
		N-deacetylranaconitine	D	Rahman & Choudhary (1995)
		delpatine		Yunusov (1991)
		14-dehydroxylappaconine	C	Yunusov (1991)

表2(续) Table 2 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterpoid alkaloid	类型 Type <sup>2)</sup>		文献 Reference
			Type <sup>2)</sup>	
C <sub>19</sub> : (23)	delphatine	B	Rahman & Choudhary (1995)	
	10-hydroxylappaconine	C	Yunusov (1991)	
	N-deacetyl lappaconitine	C	Pelletier et al. (1984)	
	lappaconidine	C	Pelletier et al. (1984)	
	lappaconine	C	Pelletier et al. (1984)	
	lappaconitine	C	Pelletier et al. (1984)	
	sepaconitine	C	Yunusov (1993)	
	leucostine	C	Usmanova et al. (1999)	
	6-O-acetylacetophenone	D	Rahman & Choudhary (1995)	
	septefine	A	Rahman & Choudhary (1999)	
	acoseptridinine	A	Rahman & Choudhary (1995)	
	acoseptridine	B	Rahman & Choudhary (1995)	
	acoseptrinine	B	Rahman & Choudhary (1995)	
	14-O-methylforesticine	A	Rahman & Choudhary (1995)	
	6-demethyl delphatine	B	Rahman & Choudhary (1995)	
	delvestidine	B	Rahman & Choudhary (1995)	
	anthranoyllycoctonine	B	Rahman & Choudhary (1995)	
	lycoctonine	B	Rahman & Choudhary (1995)	
	acoseptine	E	Usmanova et al. (1999)	
	8-O-methyllycaconitine	B	Rahman & Choudhary (1995)	
	acoseptrigine	A	Rahman & Choudhary (1997)	
	acoseptriginine	A	Rahman & Choudhary (1995)	
C <sub>20</sub> : (7)	N-acetyl sepaconitine	A	Rahman & Choudhary (1995)	
	puberaconitine	B	Rahman & Choudhary (1995)	
	anthraniloyllycoctonine	B	Rahman & Choudhary (1995)	
	anhydrolycaconitine	B	Rahman & Choudhary (1999)	
	septerine	B	Rahman & Choudhary (1999)	
	eldelidine		Yunusov (1991)	
	6-O-methyldelcorine	B	Yunusov (1991)	
	6-O-methyleldelidine		Yunusov (1991)	
	septentriodine	B	Pelletier et al. (1984)	
	septentrionine	B	Pelletier et al. (1984)	
	atisine	AI	Zinurova et al. (2000)	
	2-acetyl septentriodine	AIV	Rahman & Choudhary (1995)	
9 山地乌头* <i>A. monticola</i> Steinb.*	septatisine	AIII	Rahman & Choudhary (1995)	
	septenine	AIV	Rahman & Choudhary (1995)	
	septedine	AIII	Rahman & Choudhary (1999)	
	septedinine	AIII	Rahman & Choudhary (1999)	
	septentriodine	AV	Rahman & Choudhary (1995)	
	dihydromonticamine	C	Pelletier et al. (1984)	
	monticamine	C	Pelletier et al. (1984)	
	monticoline	D	Pelletier et al. (1984)	
	delsoline	B	Pelletier et al. (1984)	
C <sub>19</sub> : (2)	1-deoxydelsoline	B	Pelletier et al. (1984)	
	norsongorine	BI	Rahman & Choudhary (1995)	
	songorine	BI	Rahman & Choudhary (1995)	
	songorine N-oxide	BI	Rahman & Choudhary (1995)	
	songoramine	BI	Rahman & Choudhary (1995)	

表2(续) Table 2 (continued)

	分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference	
10 草地乌头*	C <sub>19</sub> : (4)	ajacine anthranoyllycoctonine lycaconitine umbrosine	B B B B	Pelletier et al. (1984) Pelletier et al. (1984) Pelletier et al. (1984) Pelletier et al. (1984)	
A. <i>umbrosum</i> (Korsh.) Kom.*					
11 吉林乌头*	C <sub>18</sub> : (11)	8-acetylexcelsine excelsine kiritine akiramine akiramidine akiradin akirine kiridine tugaconitine akiranine kirimine	C C C C C C C C D	Yunusov (1993) Sultankhodzhaev et al. (1997) Feng & Liu (1994) Tshebaeva & Sultankhodzhaev (1999) Tshebaeva et al. (1999a) Tshebaeva et al. (1999b) Yunusov (1993) Feng & Liu (1994) Tshebaeva & Sultankhodzhaev (1999)	
A. <i>kirinense</i> Nakai*					
12 细叶黄乌头*	C <sub>19</sub> : (4)	lepenine N-oxide lepenine kirinine A kirinine B kirinine C delsoline bataconine delcosine lycoctonine	C <sub>20</sub> : (5) AII AII AII AII B	Rahman & Choudhary (1995) Pelletier et al. (1984) Rahman & Choudhary (1995) Rahman & Choudhary (1995) Rahman & Choudhary (1995) Yunusov (1993) Pelletier & Joshi (1991) Yunusov (1991) Yunusov (1991)	
A. <i>barbatum</i> Pers.*					
12a 西伯利亚乌头*	C <sub>18</sub> : (2)	hispaconitine tugaconitine	C <sub>19</sub> : (3) C <sub>20</sub> : (1)	D D AII	Yunusov (1993) Yunusov (1993) Rahman & Choudhary (1995)
A. <i>barbatum</i> var. <i>hispidum</i> DC.*					
12b 牛扁*	C <sub>18</sub> : (5)	N-deacetylraconaonitine lappaconitine puberanine ranaconitine puberanidine C <sub>19</sub> : (5)	C <sub>20</sub> : (1)	D C D D D B	Pelletier et al. (1984) Pelletier et al. (1984) Pelletier et al. (1984) Pelletier et al. (1984) Pelletier et al. (1984) Rahman & Choudhary (1995)
A. <i>barbatum</i> var. <i>puberulum</i> Ledeb.*					

1)\* 表示已供药用种类。我国乌头属植物已有 76 种供药用。2) 二萜生物碱类型: A, 乌头碱型; B, 牛扁碱型; C, 高乌宁碱型; D, 冉乌宁碱型; E, 重排型。

1)\* Species medicinally used; 76 species used so far medicinally in China. 2) Type of diterpenoid alkaloids: A, aconitines; B, lycoctonines; C, lappaconines; D, ranaconines; E, rearranged type.

表3 中国乌头属乌头亚属植物中二萜生物碱成分

Table 3 Diterpenoid alkaloids in Aconitum subgenus Aconitum from China

分类群 Taxon <sup>1)</sup>		二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
<b>甘青乌头系 ser. Tangutica W. T. Wang</b>				
1 甘青乌头*	C <sub>19</sub> : (2)	heteratisine	D	Pelletier & Joshi (1991)
<i>A. tanguticum</i> (Maxim.) Stapf*		benzoylheteratisine	D	Pelletier & Joshi (1991)
	C <sub>20</sub> : (4)	tangirine	**	Wang & Liang (2002)
		tadzhaconine	AIV	Pelletier et al. (1984)
		talatizidine	AIV	Pelletier et al. (1984)
		tangutisine	AIV	Yunusov (1993)
<b>圆叶乌头系 ser. Rotundifolia Steinb.</b>				
1 圆叶乌头*	C <sub>20</sub> : (2)	atisine chloride	AI	Wang & Liang (2002)
<i>A. rotundifolium</i> Kar. & Kir.*		isoatisine	AI	Wang & Liang (2002)
2 美丽乌头*	C <sub>19</sub> : (2)	heteratisine	D	Rahman & Choudhary (1999)
<i>A. pulchellum</i> Hand.-Mazz.*		diacetylheteratisine	D	Rahman & Choudhary (1999)
<b>保山乌头系 ser. Bullatifolia W. T. Wang</b>				
1 小白撑*	C <sub>19</sub> : (3)	aconitine	A	Rahman & Choudhary (1997)
<i>A. nagarum</i> Stapf var. <i>heterotrichum</i>		deoxyaconitine	A	Rahman & Choudhary (1997)
Fletcher & Lauener*		yunaconitine	A	Rahman & Choudhary (1997)
	C <sub>20</sub> : (2)	songorine	BI	Wang & Liang (2002)
		denudatine	AI	Rahman & Choudhary (1997)
1a 无距小白撑*	C <sub>19</sub> : (3)	aconitine	A	Pelletier et al. (1984)
<i>A. nagarum</i> var. <i>heterotrichum</i>		3-deoxyaconitine	A	Pelletier et al. (1984)
<i>f. dielsianum</i> W. T. Wang*		nagarine	A	Pelletier et al. (1984)
1b 宣威乌头*	C <sub>19</sub> : (18)	vilmorrianine A	A	Dong & Li (2000)
<i>A. nagarum</i> var.		vilmorrianine B (karakoline)	A	Dong & Li (2000)
<i>lasiandrum</i> W. T. Wang*		vilmorrianine D (sachaconitine)	A	Dong & Li (2000)
		talatizidine	A	Dong & Li (2000)
		isotalatizidine	A	Dong & Li (2000)
		chasmanine	A	Dong & Li (2000)
		yunaconitine	A	Dong & Li (2000)
		aconifine	A	Pelletier et al. (1984)
		aconitine	A	Pelletier et al. (1984)
		bullatine C (14-acetylneoline)	A	Pelletier et al. (1984)
		3-deoxyaconitine	A	Pelletier et al. (1984)
		neoline	A	Pelletier et al. (1984)
		flavaconitine	A	Pelletier & Joshi (1991)
		virescenine	B	Pelletier & Joshi (1991)
		nagadine	A	Dong et al. (2000)
		14-benzoylsachaconitine	A	Dong et al. (2000)
		14-acetylneoline	A	Dong & Li (2001)
		deoxyaconitine	A	Dong & Li (2001)
	C <sub>20</sub> : (3)	songorine	B	Dong & Li (2001)
		songoramine	B	Dong & Li (2001)

表3(续) Table 3 (continued)

	分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
		denudatine	AII	Dong & Li (2001)
2 宾川乌头*	C <sub>19</sub> : (2)	aconitine	A	Pelletier et al. (1984)
<i>A. duclouxii</i> Lévl.*		duclouxine	A	Pelletier et al. (1984)
3 雷波乌头*	C <sub>19</sub> : (1)	yunaconitine	A	Yunusov (1991)
<i>A. pseudohuiliense</i> Chang ex W. T. Wang*	C <sub>20</sub> : (4)	lepedine	AII	Wang & Liang (2002)
		lepenine	AII	Wang & Liang (2002)
		lepetine	AII	Wang & Liang (2002)
		denudatine	AII	Yunusov (1991)
<b>褐紫乌头系 ser. <i>Brunnea</i> W. T. Wang</b>				
1 金阳乌头	C <sub>19</sub> : (1)	14-acetylneoline	A	Pelletier et al. (1984)
<i>A. jinyangense</i> W. T. Wang	C <sub>20</sub> : (2)	denudatine	AII	Wang & Liang (2002)
		jynosine	AII	Wang & Liang (2002)
2 褐紫乌头	C <sub>19</sub> : (2)	aconitine	A	Gao et al. (2004)
<i>A. brunneum</i> Hand.-Mazz.		benzoylaconine	A	Gao et al. (2004)
	C <sub>20</sub> : (5)	3 $\alpha$ -hydroxy-12-epi-napelline	BI	Wang & Liang (2002)
		12-epi-napelline	BI	Wang & Liang (2002)
		liangshanine	BI	Wang & Liang (2002)
		12-epi-dehydronapelline	BI	Wang & Liang (2002)
		songorine	BI	Wang & Liang (2002)
<b>显柱乌头系 ser. <i>Stylosa</i> W. T. Wang</b>				
1 滇西乌头	C <sub>18</sub> : (1)	lappaconitine	C	Rahman & Choudhary (1999)
<i>A. bulleyanum</i> Diels	C <sub>19</sub> : (6)	yunaconitine	A	Rahman & Choudhary (1999)
		crassicauline A	A	Rahman & Choudhary (1999)
		vilmorrianine C	A	Rahman & Choudhary (1999)
		lycoctonine	B	Rahman & Choudhary (1999)
		8-acetyl-14-anisoyltalatiamine	A	Jiang et al. (2002)
		14-anisoyl talatisamine	A	Jiang et al. (2002)
2 匙苞乌头*	C <sub>19</sub> : (1)	yunaconitine	A	Pelletier et al. (1984)
<i>A. spathulatum</i> W. T. Wang*				
3 膝瓣乌头(东川乌头)(大草乌)	C <sub>19</sub> : (25)	vilmorrianine A	A	Li et al. (2000)
<i>A. geniculatum</i> Fletcher & Lauener*		austroconitine B	A	Li et al. (2000)
		indaconitine	A	Li et al. (2000)
		8-acetyl-14-benzoylneoline	A	Li et al. (2000)
		8-acetyl-14-benzoylchasmanine	A	Li et al. (2000)
		isotalatizidine	A	Li et al. (2000)
		cammaconine	A	Li et al. (2000)
		14-acetylsachaconitine	A	Li et al. (2000)
		sachaconitine	A	Li et al. (2000)
		karacoline	A	Li et al. (2000)
		genicunine A	A	Wang et al. (2000a)
		genicunine B	A	Wang et al. (2000a)
		genicunine C	A	Wang et al. (2000a)

表3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
3a 爪盔膝瓣乌头 <i>A. geniculatum</i> var. <i>unguiculatum</i> W. T. Wang	C <sub>19</sub> : (2) chasmanine crassicauline A 8-deacetyllyunaconitine geniconitine talatizamine vilmorrianine C yunaconitine geniculine geniculatine A geniculatine B geniculatine C geniculatine D	A A A A A A A A A A A A A	Pelletier & Joshi (1991) Pelletier & Joshi (1991) Dong & Li (2001) Li et al. (2001) Li et al. (2001) Li et al. (2001) Li et al. (2001)
4 普格乌头 <i>A. pukeense</i> W. T. Wang	C <sub>20</sub> : (1) pukeensine	**	Wang & Liang (2002)
5 大渡乌头 <i>A. franchetii</i> Finet & Gagnep.	C <sub>19</sub> : (6) chasmaconitine chasmanine indaconitine ludaconitine talatizamine franchetine	A A A A A E	Pelletier et al. (1984) Pelletier & Joshi (1991)
6 丽江乌头* <i>A. forrestii</i> Stapf*	C <sub>18</sub> : (3) aconosine dolaconine liconosine A C <sub>19</sub> : (12) chasmamine foresticine forestine liwaconitine talatizamine yunaconitine acoforesicine acoforestine acoforestinine acoforine crassicauline A chasmaconitine	C C C C A A A A A A A A A A A	Yunusov (1993) Yunusov (1993) Yunusov (1991) Pelletier et al. (1984) Pelletier & Joshi (1991) Pelletier & Joshi (1991) Pelletier & Joshi (1991) Pelletier & Joshi (1991)
6a 毛果丽江乌头 <i>A. forrestii</i> var. <i>albovillosum</i> (Chen & Liu) W. T. Wang	C <sub>19</sub> : (3) foresaconitine 8-deacetyllyunaconitine 3 $\alpha$ , 13-dihydroxyforesaconitine	A A A	Pelletier et al. (1984) Pelletier & Joshi (1991) Pelletier & Joshi (1991)
7 康定乌头*	C <sub>19</sub> : (9) indaconitine	A	Lü et al. (1999)

表 3(续) Table 3 (continued)

	分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
A. tatsienense Finet & Gagnep.*		crassicaline A dolichotine A 8-acetyl-14-benzoyl-chasmanine yunaconitine talatisamine 8-deacetyl yunaconitine chasmanine chasmaconitine	A A A A A A A A	Lü et al. (1999) Lü et al. (1999)
8 亚东乌头*	C <sub>19</sub> : (2)	pseudaconitine	A	Pelletier et al. (1984)
A. spicatum Stapf*		bikhaconitine	A	Pelletier et al. (1984)
9 苍山乌头*	C <sub>18</sub> : (7)	delavaconitine C contortumine delavaconidine aconosine episcopalidine dolaconine	C C C C C C	Yunusov (1993) Yunusov (1993) Yunusov (1993) Pelletier & Joshi (1991) Rahman & Choudhary (1995) Pelletier & Joshi (1991)
A. contortum Finet & Gagnep.*	C <sub>19</sub> : (2) C <sub>20</sub> : (4)	cammaconine conaconitine episcopalidine contorine contorsine contortine	A A AIII AIII AIII AIII	Yunusov (1993) Pelletier & Joshi (1991) Wang & Liang (2002) Wang & Liang (2002) Wang & Liang (2002) Wang & Liang (2002)
10 直缘乌头*	C <sub>19</sub> : (20)	transconitine A transconitine B transconitine C yunaconitine crassicaline A foresaconitine C talatisamine 8-deacetyl yunaconitine geniconitine indaconitine forestine 14-acetyl talatisamine chasmanine transconitine D transconitine E N-deethyl chasmanine 8-O-ethylyunaconitine vilmorrianine A vilmorrianine C	A A A A A A A A A A A A A A A A A A A A	Zheng et al. (1997) Zheng et al. (1997) Chen et al. (2003a) Chen et al. (2003a) Chen et al. (2003a) Chen et al. (2003a) Chen et al. (2003a)
A. transsectum Diels*				

表 3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
	chasmaconitine	A	Chen et al. (2003a)
<b>岩乌头系 ser. <i>Racemulosa</i> W. T. Wang</b>			
1 彭州岩乌头(岩乌) <i>A. racemulosum</i> Franch. var. <i>pengzhouense</i> W. J. Zhang & G. H. Chen	C <sub>19</sub> : (15) condelphine isotalatizidine 14-O-acetylviresscenine viresscenine anthranoylllycoctonine talatisamine isotalatizidine sachaconitine nevadenine pseudacolline lycoctonine 14-acetylviresscenine 1-epi-chasmanine vilmorrianine D pseudacolline C <sub>20</sub> : (7) racemuloline A racemuloline B kusnezoline racemulodine 	A A B B A A A A A B B B A A A A ** ** ** AIII ** AII AI	Peng et al. (2000c) Peng et al. (2000d) Peng et al. (2000c) Peng et al. (2000c) Peng et al. (2000c) Peng et al. (2000d) Peng et al. (2000a) Peng et al. (2000d) Peng et al. (2000d) Peng et al. (2000d) Peng et al. (2002) Peng et al. (2002c) Wang & Liang (2002) Wang et al. (2002) Wang et al. (2000b) Peng et al. (2001) Peng et al. (2000b)
<b>蔓乌头系 ser. <i>Volubilia</i> Steinb.</b>			
1 瓜叶乌头* <i>A. hemsleyanum</i> Pritz.*	C <sub>19</sub> : (9) hemsleyanaine chasmanine indaconitine talatisamine guayewuanine A guayewuanine B (yunaconitine) hemsleyatine yunaconitine	A A A A A A A	Rahman & Choudhary (1997) Rahman & Choudhary (1997) Rahman & Choudhary (1997) Rahman & Choudhary (1997) Pelletier & Joshi (1991) Pelletier & Joshi (1991) Zhou et al. (2003) Zhou et al. (2003)
1a 白花瓜叶乌头 <i>A. hemsleyanum</i> var. <i>leucanthum</i> P. Guo & M. R. Jia	C <sub>19</sub> : (7) leueandine 13,15-dideoxyaconitine ezochasmanine crassicaudine franchetine potanisine F potanisine G leucantines A, B, C, D	E A A A E B B A	Chen et al. (2003b) Chen et al. (2003b)
1b 彭什藤乌 <i>A. hemsleyanum</i> var.	C <sub>19</sub> : (18) 1-epicrassicaudine indaconitine	A A	Rahman & Choudhary (1997) Rahman & Choudhary (1997)

表3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
<i>pengshiene</i> W. J. Zhang	chasmanconitine	A	Rahman & Choudhary (1997)
	ludaconitine	A	Rahman & Choudhary (1997)
	chasmanine	A	Rahman & Choudhary (1997)
	talatisamine	A	Rahman & Choudhary (1997)
	frechitine	A	Rahman & Choudhary (1997)
	franchetine	E	Rahman & Choudhary (1995)
	13-dehydroxyindaconitine	A	Peng et al. (1991)
	crassicaudine	A	Peng et al. (1991)
	ezochasmanine	A	Peng et al. (1991)
	14-debenzoylfranchetine	E	Peng et al. (1991)
	pengshenine A	A	Wang & Liang (2002)
	pengshenine B	A	Wang & Liang (2002)
	13-deoxyludaconitine	A	Peng et al. (2000b)
	8-deactylsungpaconitine	A	Peng et al. (2000b)
	6-epiforsticine	A	Peng et al. (2002)
	13-dehydroxylludaconitine	A	Peng et al. (2000e)
1c 拳距瓜叶乌头*	C <sub>19</sub> : (10)	hemsleyasine	A Xu & Wang (1997)
<i>A. hemsleyanum</i> var. <i>circinatum</i>		hemsleyanidine	A Xu et al. (1996a)
W. T. Wang*		isohemsleyanidine	A Xu et al. (1996a)
		talatizamine	A Xu et al. (1996a)
		hemsleyadine	A Xu et al. (1996b)
		crassicauline A	A Pelletier et al. (1984)
		chasmanine	A Pelletier et al. (1984)
		karakoline	A Pelletier et al. (1984)
		pseudaconitine	A Pelletier et al. (1984)
		yunaconitine	A Pelletier et al. (1984)
2 粗茎乌头*	C <sub>19</sub> : (10)	chasmanine	A Pelletier et al. (1984)
<i>A. crassicaule</i> W. T. Wang*		crassicaulidine	A Pelletier et al. (1984)
		crassicauline A	A Pelletier et al. (1984)
		crassicaulinsine	A Pelletier et al. (1984)
		yunaconitine	A Pelletier et al. (1984)
		crassicaudine	A Pelletier & Joshi (1991)
		crassicausine	A Pelletier & Joshi (1991)
		crassicautine	A Pelletier & Joshi (1991)
		foresaconitine	A Pelletier & Joshi (1991)
		forestine	A Pelletier & Joshi (1991)
	C <sub>20</sub> : (1)	crassicauline B	AIV Wang & Liang (2002)
3 滇南乌头*	C <sub>19</sub> : (13)	austroconitine A	A Pelletier & Joshi (1991)
<i>A.austroyunnanense</i> W. T. Wang*		austroconitine B	Pelletier & Joshi (1991)
		condelphine	A Pelletier & Joshi (1991)
		8-deacetyllyunaconitine	A Pelletier & Joshi (1991)
		isotalatizidine	A Pelletier & Joshi (1991)

表3(续) Table 3 (continued)

		分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
4 黄草乌*			talatizamine	A	Pelletier & Joshi (1991)
			talatizidine	A	Pelletier & Joshi (1991)
			vilmorrianine A	A	Pelletier & Joshi (1991)
			vilmorrianine B (karakoline)	A	Pelletier & Joshi (1991)
			vilmorrianine C	A	Pelletier & Joshi (1991)
			vilmorrianine D	A	Pelletier & Joshi (1991)
			yunaconitine	A	Pelletier & Joshi (1991)
			8-deactylvilmorrianine A	A	Yunusov (1993)
4a 深裂黄草乌		C <sub>19</sub> : (17)	acoforine	A	Rahman & Choudhary (1997)
	<i>A. vilmorinianum</i> Kom.*		columbidine	A	Rahman & Choudhary (1997)
			yunaconitine	A	Rahman & Choudhary (1997)
			sachaconitine	A	Rahman & Choudhary (1997)
			14-O-acetylsachaconitine	A	Rahman & Choudhary (1997)
			vilmorrianine A	A	Pelletier et al. (1984)
			vilmorrianine B	A	Pelletier et al. (1984)
			vilmorrianine C	A	Pelletier et al. (1984)
			vilmorrianine D	A	Pelletier et al. (1984)
			yunaconitine	A	Pelletier et al. (1984)
			talatizidine	A	Yunusov (1993)
			isotalatizidine	A	Yunusov (1993)
			talatisamine	A	Yunusov (1993)
			karakoline	A	Yunusov (1993)
		C <sub>20</sub> : (2)	vilmordine	**	Wang & Liang (2002)
			vilmorianone	AIII	Wang & Liang (2002)
4b 展毛黄草乌		C <sub>19</sub> : (1)	deoxyaconitine	A	Zhang et al. (1997)
	<i>A. vilmorinianum</i> var.	C <sub>20</sub> : (2)	denudatine	AII	Wang et al. (2002)
	<i>altifidum</i> W. T. Wang		vilmorianone	AIII	Wang et al. (2002)
			patentine	A	Yunusov (1993)
			indaconitine	A	Yunusov (1993)
	<i>A. vilmorinianum</i> var.		yunaconitine	A	Yunusov (1993)
	<i>patentipilum</i> W. T. Wang		talatisamine	A	Yunusov (1993)
			franchetine	E	Yunusov (1993)
			chasmaconitine	A	Yunusov (1993)
			crassicauline A	A	Yunusov (1993)
			bikhaconine	A	Yunusov (1993)
5 玉龙乌头*		C <sub>18</sub> : (1)	8-deoxy-14-dehydroaconosine	A	Pelletier & Joshi (1991)
	<i>A. staphianum</i> Hand.-Mazz.*	C <sub>19</sub> : (3)	crassicauline A	A	Pelletier & Joshi (1991)
			talatizamine	A	Pelletier & Joshi (1991)
			yunaconitine	A	Pelletier & Joshi (1991)
6 拟玉龙乌头*		C <sub>18</sub> : (2)	aconosine	A	Pelletier & Joshi (1991)
	<i>A. pseudostaphianum</i>		8-deoxy-14-dehydroaconosine	A	Pelletier & Joshi (1991)
	W. T. Wang*	C <sub>19</sub> : (9)	14-benzoyl-8-O-methylaconine	A	Rahman & Joshi (1999)

表3(续) Table 3 (continued)

	分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
7 西南乌头*	C <sub>19</sub> : (5)	aconitine	A	Rahman & Choudhary (1999)
		deoxyaconitine	A	Rahman & Choudhary (1999)
		penduline	A	Rahman & Choudhary (1999)
		yunaconitine	A	Rahman & Choudhary (1999)
		neolinine	A	Rahman & Choudhary (1999)
		15 $\alpha$ -hydroxyneoline	A	Rahman & Choudhary (1999)
		neoline	A	Rahman & Choudhary (1999)
		talatisamine	A	Rahman & Choudhary (1999)
7 西南乌头*	C <sub>19</sub> : (5)	liaconitine A	A	Yang et al. (1999)
<i>A. episcopale</i> Lévl.*		liaconitine B	A	Yang et al. (1999)
		liaconitine C	A	Yang et al. (1999)
		talatisamine	A	Rahman & Choudhary (1995)
		14-acetyltaelatisamine	A	Rahman & Choudhary (1995)
8 弯喙乌头*	C <sub>18</sub> : (3)	episcopalidine	AII	Yunusov (1993)
<i>A. campylorrhynchum</i>		songorine	BI	Yunusov (1993)
Hand.-Mazz.*		heterophylloidine	AIII	Yunusov (1993)
		deacetylphylloidine	AIII	Yunusov (1993)
8 弯喙乌头*	C <sub>18</sub> : (3)	8-acetyladolaconine	C	Yunusov (1993)
<i>A. campylorrhynchum</i>		aconosine	C	Yunusov (1993)
Hand.-Mazz.*		dolaconine	C	Yunusov (1993)
9 松潘乌头*	C <sub>19</sub> : (6)11	8-deacetyllyunaconitine	A	Pelletier & Joshi (1991)
<i>A. sungpanense</i> Hand.-Mazz.*		8-acetyl-14-benzoylchasmanine	A	Pelletier & Joshi (1991)
		aconitine	A	Pelletier & Joshi (1991)
		chasmanine	A	Pelletier & Joshi (1991)
		crassicauline A	A	Pelletier & Joshi (1991)
		13,15-dideoxyaconitine	A	Pelletier & Joshi (1991)
		foresaconitine	A	Pelletier & Joshi (1991)
		sungpanconitine	A	Pelletier & Joshi (1991)
		talatizamine	A	Pelletier & Joshi (1991)
		vilmorrianine A	A	Pelletier & Joshi (1991)
		yunaconitine	A	Yunusov (1991)
10 宽叶蔓乌头*	C <sub>19</sub> : (2)	mesaconitine	A	Pelletier et al. (1984)
<i>A. szukinii</i> Turcz.*		neoline	A	Pelletier et al. (1984)
	C <sub>20</sub> : (3)	szukinine	AIII	Wang & Liang (2002)
		szukidine	AIII	Wang & Liang (2002)
		szukitine	AIII	Wang & Liang (2002)
11 蔓乌头*	C <sub>19</sub> : (1)	aconitine	A	Yanusov (1993)
<i>A. volubile</i> Pall. & Koelle*	C <sub>20</sub> : (2)	napelline	B	Wang & Liang (2002)
		songorine	B	Wang & Liang (2002)
<b>乌头系 ser. <i>Inflata</i> Steinb.</b>				
1 薄叶乌头	C <sub>18</sub> : (1)	aconosine	C	Pelletier & Joshi (1991)
<i>A. fischeri</i> Reichb.	C <sub>19</sub> : (3)	aconitine	A	Pelletier et al. (1984)

表3(续) Table 3 (continued)

	分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
2 大苞乌头 <i>A. raddeanum</i> Regel	C <sub>19</sub> : (2)	jesaconitine	A	Pelletier et al. (1984)
		talatizamine	A	Pelletier et al. (1984)
3 梨山乌头 <i>A. fukutomei</i> Hayata	C <sub>19</sub> : (9)	sachaconitine	A	Rahman & Choudhary (1997)
		14-acetyl sachaconitine	A	Rahman & Choudhary (1997)
4 锐裂乌头 <i>A. kojimae</i> Ohwi ex Tamura	C <sub>20</sub> : (1)	10-hydroxyneoline	A	Yunusov (1993)
		14-O-acetyl-10-hydroxyneoline	A	Yunusov (1993)
		neoline	A	Yunusov (1993)
		14-acetylneoline	A	Yunusov (1993)
		15 $\alpha$ -hydroxyneoline	A	Yunusov (1993)
		senbusine A	A	Yunusov (1993)
		isotalatizidine	A	Yunusov (1993)
		mesaconitine	A	Yunusov (1993)
		aconitine	A	Pelletier et al. (1984)
		lassiocarpine	AII	Wang & Liang (2002)
5 乌头* <i>A. carmichaeli</i> Debx.*	C <sub>19</sub> : (41)	8-deacetyl mesaconitine	A	Rahman & Choudhary (1995)
		aldohypaconitine	A	Rahman & Choudhary (1997)
		deoxyaconitine	A	Han et al. (1997)
		neojiangyouaconitine	A	Han et al. (1997)
		14-acetyl talatizamine	A	Pelletier et al. (1984)
		aconitine	A	Pelletier et al. (1984)
		14-benzoyl mesaconine	A	Pelletier et al. (1984)
		fuziline	A	Pelletier et al. (1984), Pelletier & Joshi (1991)
		hokbusine A	A	Pelletier et al. (1984)
		hokbusine B	A	Pelletier et al. (1984)
		15 $\alpha$ -hydroxyneoline	A	Pelletier et al. (1984)
		hypaconitine	A	Pelletier et al. (1984), Pelletier & Joshi (1991)
		isodelphinine	A	Pelletier et al. (1984)
		isotalatizidine	A	Pelletier et al. (1984)
		karakoline	A	Pelletier et al. (1984), Pelletier & Joshi (1991)
		neoline	A	Pelletier et al. (1984)
		senbusine A	A	Pelletier et al. (1984)
		senbusine B	A	Pelletier et al. (1984)
		talatizamine	A	Pelletier et al. (1984)
		14-benzoylaconine	A	Pelletier & Joshi (1991)
		14-benzoylhypaconine	A	Pelletier & Joshi (1991)
		lipoaconitine	A	Pelletier & Joshi (1991)
		lipo-3-deoxyaconitine	A	Pelletier & Joshi (1991)
		lipohypaconitine	A	Pelletier & Joshi (1991)

表3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
	lipomesaconitine	A	Pelletier & Joshi (1991)
	mesaconitine	A	Pelletier & Joshi (1991)
	aconitine	A	Pelletier & Joshi (1991)
	beiwutine	A	Pelletier & Joshi (1991)
	deoxyaconitine	A	Pelletier & Joshi (1991)
	jiangyouaconitine	A	Yunusov (1993)
	benzoylmesaconitine	A	Yunusov (1993)
	8-O-cinnamoylneoline	A	Masanori et al. (2003)
	14-O-cinnamoylneoline	A	Shim et al. (2003a)
	14-O-anisoylneoline	A	Shim et al. (2003a)
	14-O-veratroylneoline	A	Shim et al. (2003a)
	lipo-14-O-anisoylbikhaconine	A	Shim et al. (2003a)
	foresaconitine	A	Shim et al. (2003a)
	crassicauline A	A	Shim et al. (2003a)
	14-O-acetylneoline	A	Shim et al. (2003a)
	senbusine C	A	Pelletier et al. (1984)
C <sub>20</sub> : (4)	songoramine	BI	Wang & Liang (2002)
	songorine	BI	Wang & Liang (2002)
	ignavine	AV	Bessonova & Saidkhodzhaeva (2000)
	chuanfunine	BI	Wang & Liang (2002)
6 北乌头*	C <sub>19</sub> : (33) aconifine	A	Rahman & Choudhary (1999)
<i>A. kusnezoffii</i> Reichb.*	14-benzoylaconine	A	Rahman & Choudhary (1999)
	14-benzoylmesaconine	A	Rahman & Choudhary (1999)
	neoline	A	Rahman & Choudhary (1999)
	15 $\alpha$ -hydroxyneoline	A	Rahman & Choudhary (1999)
	chasmanine	A	Rahman & Choudhary (1999)
	talatizamine	A	Rahman & Choudhary (1999)
	foresticine	A	Rahman & Choudhary (1999)
	lycoctonine	B	Rahman & Choudhary (1999)
	anthranoylllycoctonine	B	Rahman & Choudhary (1999)
	beiwudine	A	Peng et al. (1991)
	3-acetylaconitine	A	Ren et al. (1999)
	3-acetylmesaconitine	A	Ren et al. (1999)
	3-acetylaconifine	A	Ren et al. (1999)
	isotalatidisidine	A	Rahman & Choudhary (1999)
	talatisidine	A	Rahman & Choudhary (1999)
	10-hydroxyneoline	A	Rahman & Choudhary (1999)
	6-epichasmanine	A	Li & Wang (1996)
	8-OEt-14-benzoylmesaconine	A	Yu & Jia (2000)
	beiwucine	A	Yu & Jia (2000)
	aconitine	A	Pelletier et al. (1984)

表3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
	3-deoxyaconitine	A	Pelletier et al. (1984)
	hypaconitine	A	Pelletier et al. (1984)
	mesaconitine	A	Zinurova et al. (2001)
	acsonine	A	Zinurova et al. (2001)
	beiwutine	A	Zinurova et al. (2001)
	deoxyaconitine	A	Zinurova et al. (2001)
	mesaconine	A	Zinurova et al. (2001)
	6-epiforsticinae	A	Zinurova et al. (2001)
	hemsleyanidine	A	Li & Wang (1999)
	isohemsleyanidine	A	Li & Wang (1999)
	beiwudine	F	Wang et al. (1998)
	candidine	A	Rahman & Choudhary (1995)
6a 伏毛北乌头* <i>A. kusnezoffii</i> var. <i>crispulum</i> W. T. Wang*	C <sub>20</sub> : (5) beiwusine A	AI	Wang & Liang (2002)
	beiwusine B	AI	Wang & Liang (2002)
	denudatine	AII	Wang & Liang (2002)
	kusnezoline(no name)	**	Wang & Liang (2002)
	lepenine	AII	Zinurova et al. (2001)
7 鹅绿乌头* <i>A. jaluense</i> Kom.*	C <sub>19</sub> : (5) mesaconitine	A	Yunusov (1993)
	hypaconitine	A	Yunusov (1993)
	deoxyaconitine	A	Yunusov (1993)
	aconitine	A	Yunusov (1993)
	neoline	A	Yunusov (1993)
	C <sub>19</sub> : (13) deoxyaconitine	A	Yunusov (1993)
	hypaconitine	A	Rahman & Choudhary (1995)
	aconitine	A	Rahman & Choudhary (1995)
	mesaconitine	A	Rahman & Choudhary (1995)
	acetylthalatisamine	A	Rahman & Choudhary (1995)
8 敦化乌头 <i>A. dunhuense</i> H. S. Li	talatisamine	A	Rahman & Choudhary (1995)
	neoline	A	Rahman & Choudhary (1995)
	benzoylmesaconine	A	Rahman & Choudhary (1995)
	jaluensine	A	Rahman & Choudhary (1995)
	lipomesaconitine	A	Shim et al. (2003b)
	lipohypaconitine	A	Shim et al. (2003b)
	15'-hydroxyneoline	A	Shim et al. (2003b)
	hokbusine A	A	Shim et al. (2003b)
	C <sub>20</sub> : (1) napelline	BI	Shim et al. (2003b)
	C <sub>18</sub> : (1) aconosine	C	Rahman & Choudhary (1995)

表3(续) Table 3 (continued)

	分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
9 长白乌头		mesaconitine	A	Rahman & Choudhary (1995)
	C <sub>19</sub> : (6)	3-acetylmesaconitine	A	Yunusov (1993)
<i>A. tschangbaischanense</i>		tschangbaischanitine	A	Yunusov (1993)
S. H. Li & Y. H. Huang		nicotine	A	Yunusov (1993)
		hypaconitine	A	Yunusov (1993)
		mesaconitine	A	Yunusov (1993)
		8-O-ethyl-14-benzoylmesaconine	A	Yunusov (1993)
	C <sub>20</sub> : (1)	songorine	BI	Yunusov (1993)
<b>兴安乌头系 ser. <i>Ambigua</i> Steinb.</b>				
1 马耳山乌头*	C <sub>18</sub> : (4)	delavaconitine C	A	Yunusov (1991)
<i>A. delavayi</i> Franch.*		delavaconitine D	A	Yunusov (1991)
		delavaconitine	A	Pelletier et al. (1984)
		delavaconinine	A	Pelletier & Joshi (1991)
		delavaconitine E	A	Pelletier & Joshi (1991)
	C <sub>19</sub> : (2)	delavaconine	A	Yunusov (1991)
		yunaconitine	A	Pelletier et al. (1984)
2 长序乌头	C <sub>19</sub> : (11)	dolichotine D	A	Yunusov (1993)
<i>A. dolichostachyum</i>		dolichotine E	A	Yunusov (1993)
W. T. Wang		yunaconitine	A	Yunusov (1993)
		8-deacetyluyaconitine	A	Yunusov (1993)
		crassicauline A	A	Yunusov (1993)
		talatisamine	A	Yunusov (1993)
		columbidine	A	Yunusov (1993)
		cammaconine	A	Yunusov (1993)
		dolichotine A	A	Pelletier & Joshi (1991)
		dolichotine B	A	Pelletier & Joshi (1991)
		dolichotine C	A	Pelletier & Joshi (1991)
3 工布乌头*	C <sub>19</sub> : (10)	kongboensine	A	Chen et al. (1994)
<i>A. kongboense</i> Lauener*		guayewuanine A	A	Chen et al. (1994)
		indaconitine	A	Chen et al. (1994)
		talatisamine	A	Chen et al. (1994)
		vilmorrianine A	A	Pelletier et al. (1984)
		kongboentine A	A	Ping (2004)
		kongboentine B	A	Ping (2004)
		pyrochasmaconitine	C	Rahman & Choudhary (1997)
		pyrocassicauine A	C	Rahman & Choudhary (1997)
		14-benzoyltalatisamine	A	Rahman & Choudhary (1997)
3a 展毛工布乌头	C <sub>19</sub> : (6)	chasmaconitine	A	Yunusov (1993)
<i>A. kongboense</i> var.		talatisamine	A	Yunusov (1993)
<i>villosum</i> W. T. Wang		kongboenine	A	Yunusov (1993)
		pyrochasmaconitine	C	Pelletier & Joshi (1991)
		pyrocassicauine A	C	Pelletier & Joshi (1991)
		14-benzoyltalatisamine	A	Pelletier & Joshi (1991)

表3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>		二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
4 拟膝瓣乌头	C <sub>19</sub> : (6)	chasmanine	A	Pelletier & Joshi (1991)
<i>A. pseudogeniculatum</i>		crassiculine A	A	Pelletier & Joshi (1991)
W. T. Wang		foresaconitine	A	Pelletier & Joshi (1991)
		talatizamine	A	Pelletier & Joshi (1991)
		yunaconitine	A	Pelletier & Joshi (1991)
		vilmorrianine C	A	Pelletier & Joshi (1991)
5 凉山乌头*	C <sub>20</sub> : (1)	denudatine	AI	Pelletier & Joshi (1991)
<i>A. liangshanicum</i> W. T. Wang*	C <sub>19</sub> : (4)	aconitine	A	Yunusov (1993)
		aconine	A	Yunusov (1993)
		neoline	A	Yunusov (1993)
		senbusine A	A	Yunusov (1993)
6 贡嘎乌头*	C <sub>20</sub> : (6)	12-epi-lucidusculine	BI	Wang & Liang (2002)
<i>A. liljestrandii</i> Hand.-Mazz.*		liangshanine	BI	Wang & Liang (2002)
		liangshanone	BI	Wang & Liang (2002)
		12-epinapelline	BI	Wang & Liang (2002)
		songorine	BI	Pelletier et al. (1984)
		12-epi-dehydronapelline	BI	Yunusov (1993)
7 展花乌头*	C <sub>19</sub> : (18)	liljestrandinine	A	Xie et al. (2003)
<i>A. chasmanthum</i> Stapf*		liljestrandisine	A	Xie & Wang (2004)
		N-deethyltalatismine	A	Xie et al. (2003)
		chasmaconitine	A	Xie et al. (2003)
		forestine	A	Xie et al. (2003)
		pengshenine B	A	Xie et al. (2003)
		cammaconine	A	Xie et al. (2003)
		6-epi-foresticine	A	Xie et al. (2003)
		indaconitine	A	Xie et al. (2003)
		yunaconitine	A	Xie et al. (2003)
		chasmanine	A	Xie et al. (2003)
		14-debenzoylfranchetine	E	Xie et al. (2003)
		pseudaconine	A	Xie et al. (2003)
		chasmanine	A	Xie et al. (2003)
		ludaconitine	A	Xie et al. (2003)
		8-deacetylunaconitine	A	Xie et al. (2003)
		talatismine	A	Xie et al. (2003)
		genicunine A	A	Xie et al. (2003)
准噶尔乌头系 ser. <i>Grandituberosa</i> Steinb.	C <sub>19</sub> : (6)	neoline	A	Pelletier & Joahi (1991)
1 准噶尔乌头(新疆草乌)*	C <sub>19</sub> : (2)	aconitine	A	Pelletier et al. (1984)

表3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
<i>A. soongaricum</i> Stapf*	neoline	A	Pelletier et al. (1984)
C <sub>20</sub> : (11)	12-acetylnapelline	BI	Wang & Liang (2002)
	12-acetylnapelline N-oxide	BI	Wang & Liang (2002)
	15-acetylsongoramine	BI	Wang & Liang (2002)
	15-acetylsongorine	BI	Wang & Liang (2002)
	napelline	BI	Wang & Liang (2002)
	napelline N-oxide	BI	Wang & Liang (2002)
	norsongorine	BI	Wang & Liang (2002)
	songoramine	BI	Wang & Liang (2002)
	songorine	BI	Wang & Liang (2002)
	11-epi-dehynapelline	BI	Wang & Liang (2002)
	12-epi-napelline	BI	Wang & Liang (2002)
2 多根乌头*	C <sub>18</sub> : (2)	A	Pelletier & Joshi (1991)
<i>A. karakolicum</i> Rapaics*	monticamine	B	Pelletier et al. (1984)
	monticoline		
C <sub>19</sub> : (15)	karakonitine		Rahman & Choudhary (1999)
	secokaraconitine	E	Sultankhudzhaev et al. (2002)
	3-deoxyaconitine	A	Rahman & Choudhary (1999)
	indaconitine	A	Rahman & Choudhary (1999)
	chasmaconitine	A	Rahman & Choudhary (1999)
	karakanine	A	Rahman & Choudhary (1995)
	aconifine	A	Pelletier et al. (1984)
	aconitine	A	Pelletier et al. (1984)
	1-benzoylkarasamine	A	Pelletier et al. (1984)
	delsoline	B	Pelletier et al. (1984)
	karakolidine	A	Pelletier et al. (1984)
	karakoline	A	Pelletier et al. (1984)
	karasamine	A	Pelletier et al. (1984)
	cammaconine	A	Sultankhudzhaev et al. (2002)
	neoline	A	Pelletier et al. (1984)
C <sub>20</sub> : (9)	12-acetylnapelline	BI	Wang & Liang (2002)
	acofine	BI	Wang & Liang (2002)
	dehydrosongorine	BI	Wang & Liang (2002)
	12-epinapelline	BI	Wang & Liang (2002)
	karakonine	BI	Wang & Liang (2002)
	napelline	BI	Wang & Liang (2002)
	songoramine	BI	Wang & Liang (2002)
	songorine	BI	Wang & Liang (2002)
	karakomine	BI	Yunusov (1993)
2a 展毛多根乌头	C <sub>19</sub> : (6)	A	Pelletier & Joshi (1991)
<i>A. karakolicum</i> var.	benzoylaconine	A	Pelletier & Joshi (1991)
<i>patentipilum</i> W. T. Wang	karasamine	A	Pelletier & Joshi (1991)
	aconitine	A	Pelletier & Joshi (1991)
	deoxyaconitine	A	Pelletier & Joshi (1991)

表3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
3 伊犁乌头 <i>A. talassicum</i> Popov. var. <i>villosulum</i> W. T. Wang	karakoline	A	Pelletier & Joshi (1991)
	neoline	A	Pelletier & Joshi (1991)
	C <sub>19</sub> : (3) talassicmine A	A	Rahman & Choudhary (1997)
	talassicmine B	B	Rahman & Choudhary (1997)
	talassicmine C	A	Rahman & Choudhary (1997)
	cammaconine	A	Rahman & Choudhary (1997)
4 林地乌头* <i>A. nemorum</i> M. Pop.*	aconorine	A	Rahman & Choudhary (1997)
	songrine	BI	Rahman & Choudhary (1997)
	C <sub>19</sub> : (5) 14-benzoyltalatizamine	A	Rahman & Choudhary (1999)
	14-acetyltaлизamine	A	Pelletier et al. (1984)
	talatizamine	A	Pelletier et al. (1984)
	1-epi-deacetylaconitine	A	Wei et al. (2000)
短柄乌头系 ser. <i>Brachypoda</i> W. T. Wang	neoline	A	Pelletier et al. (1984)
	C <sub>20</sub> : (2) songrine	BI	Wang & Liang (2002)
	12-epi-napelline	BI	Wang & Liang (2002)
	1 多裂乌头* <i>A. polyschistum</i> Hand.-Mazz.*		
	C <sub>19</sub> : (8) aconitine	A	Pelletier & Joshi (1991)
2 伏毛铁棒锤* <i>A. flavum</i> Hand.-Mazz.*	14-benzoylaconine	A	Pelletier & Joshi (1991)
	14-benzoyl-3-deoxyaconine	A	Pelletier & Joshi (1991)
	deoxyaconitine	A	Pelletier & Joshi (1991)
	polyschistine A	A	Pelletier & Joshi (1991)
	polyschistine B	A	Pelletier & Joshi (1991)
	polyschistine C	A	Pelletier & Joshi (1991)
3 铁棒锤* <i>A. pendulum</i> Busch*	polyschistine D	A	Pelletier & Joshi (1991)
	C <sub>19</sub> : (10) 3-acetylaconitine	A	Pelletier et al. (1984)
	aconitine	A	Pelletier et al. (1984)
	flavaconitine	A	Pelletier et al. (1984)
	N-acetylflavaconitine	A	Pelletier & Joshi (1991)
	benzoylaconine	A	Pelletier & Joshi (1991)
3 铁棒锤* <i>A. pendulum</i> Busch*	1-demethylhapaconitine	A	Pelletier & Joshi (1991)
	deoxyaconitine	A	Pelletier & Joshi (1991)
	flavaconidine	A	Pelletier & Joshi (1991)
	flavaconijine	A	Pelletier & Joshi (1991)
	neoline	A	Pelletier & Joshi (1991)
	C <sub>20</sub> : (3) 1-epinapelline	BI	Wang & Liang (2002)
3 铁棒锤* <i>A. pendulum</i> Busch*	flavadine	BI	Wang & Liang (2002)
	flavamine	BI	Wang & Liang (2002)
	C <sub>19</sub> : (8) 2-hydroxydeoxyaconitine	A	Zhang et al. (1997b)
	noeline	A	Zhang et al. (1997b)
	3-acetylaconitine	A	Pelletier et al. (1984)
	aconitine	A	Pelletier et al. (1984)
3 铁棒锤* <i>A. pendulum</i> Busch*	3-deoxyaconitine	A	Pelletier et al. (1984)
	hypaconitine	A	Pelletier et al. (1984)

表3(续) Table 3 (continued)

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference
	penduline	A	Pelletier et al. (1984)
	szechenyine	A	Pelletier & Joshi (1991)
	deoxyaconitine	A	Pelletier et al. (1984)
C <sub>20</sub> : (5)	12-epiacetyldehydro-		
	lucidusculine	BI	Wang & Liang (2002)
	dehydronapelline	BI	Wang & Liang (2002)
	12-epiacetyldehydronapelline	BI	Wang & Liang (2002)
	dehydrolucidusculline	BI	Wang & Liang (2002)
	songorine	BI	Pelletier & Joshi (1991)
4 黄花乌头(关白附)*	C <sub>19</sub> : (1) condelphine	A	Rahman & Choudhary (1999)
<i>A. coreanum</i> (Lévl.)	C <sub>20</sub> : (21) acoridine	AV	Wang & Liang (2002)
Rapaics*	13-acetyl-14-hydroxy-		
	2-propionyl hetisine	AV	Wang & Liang (2002)
	atisine chloride	AI	Wang & Liang (2002)
	coriphine	AIII	Wang & Liang (2002)
	coryphidine	AIII	Wang & Liang (2002)
	guan-fu base A	AV	Wang & Liang (2002)
	guan-fu base F	AV	Wang & Liang (2002)
	guan-fu base F N-oxide	AV	Wang & Liang (2002)
	guan-fu base G	AV	Wang & Liang (2002)
	guan-fu base H	**	Rahman & Choudhary (1999)
	guan-fu base K	**	Wang & Liang (2002)
	guan-fu base O	AV	Wang & Liang (2002)
	guan-fu base Y	AV	Wang & Liang (2002)
	guan-fu base Z	AV	Wang & Liang (2002)
	guan-fu base Z N-oxide	AV	Wang & Liang (2002)
	isoatrisine	AI	Wang & Liang (2002)
	hetisinone	AV	Pelletier et al. (1984)
	2,11,13-triacetyl-14-hydroxyheti- sine	AV	Bessonora (1999)
	tadzhaconine	AV	Pelletier et al. (1984)
	talatizine	AV	Pelletier et al. (1984)
	tangutisine	AV	Pelletier et al. (1984)
5 拟黄花乌头*	C <sub>19</sub> : (1) condelphine	A	Pelletier et al. (1984)
<i>A. anthoroideum</i> DC.*			

1)\* 表示已供药用种类。我国乌头属植物已有76种供药用。2) 二萜生物碱类型: A, 乌头碱型; B, 牛扁碱型; C, 高乌宁碱型; D, 内酯型; E, 7,17次裂型; AI, 阿替生型; AII, 光翠雀碱型; AIII, 海替定型; AV, 海替生型; BI, 纳哌啉型; \*\*其他类型(罕见)。

1)\* Species medicinally used; 76 species used so far medicinally in China. 2) Type of diterpenoid alkaloids: A, aconitines; B, lycocotonines; C, lappaconines; D, lactones; E, 7,17-seco type; AI, atisines; AII, denudatines; AIII, hetidines; AV, hetisines; BI, napellines; \*\* other types (rare).

表4 乌头属露蕊亚属植物中二萜生物碱成分

Table 4 Diterpenoid alkaloids in *Aconitum* subgen. *Gymnaconitum* (Stapf) Rapaics from China

分类群 Taxon <sup>1)</sup>	二萜生物碱 Diterploid alkaloid	类型 Type <sup>2)</sup>	文献 Reference	
1 露蕊乌头 <sup>*</sup> <i>A. gymnanthrum</i> Maxim.	C <sub>18</sub> : (1) C <sub>19</sub> : (9)	ranaconitine 14-acetyl-8-O-methyltalatisamine acoferine columbidine aconitine talatizidine isotalatizidine gymnaconitine 1-O-methylgymnaconitine talatizamine C <sub>20</sub> : (2) gymnandine atisine HCl	B A A A A A A A A AII AI	Rahman & Choudhary (1995) Rahman & Choudhary (1995) Rahman & Choudhary (1995) Rahman & Choudhary (1995) Rahman & Choudhary (1995) Pelletier & Joshi (1991) Pelletier & Joshi (1991) Pelletier & Joshi (1991) Yunusov (1993)

1) \*表示已供药用。2) 二萜生物碱类型: A, 乌头碱; B, 牛扁碱型; AI, 阿替生型; AII, 光翠雀碱型。

1) \*Species medicinally used. 2) Type of diterpenoid alkaloids: A, aconitines; B, lycocotonines; AI, atisines; AII, denudatines.

## 2.2 酯化程度和取代位置

这方面信息具有重要的分类学价值。酯化程度有单酯、双酯、多酯之分。其种类的复杂程度则由醋酸酯(OAc)到苯甲酸酯(OBz)、大茴香酸酯(OAs)、藜芦酸酯(OVr)和邻氨基苯甲酸衍生物酯等来决定。在二萜生物碱中, 这些酯基的取代位置也颇具特征性: OAc、OBz和OAs酯基几乎全出现在乌头碱型中, 且集中分布于乌头亚属植物。而其取代位置最常见的是C-8和C-14上, 且构成双酯的主体部分。邻氨基苯甲酸衍生物酯几乎全部存在于牛扁碱型中, 且主要分布于牛扁亚属和翠雀属植物中, 显示出牛扁亚属和翠雀属植物的相似性。邻氨基苯甲酸衍生物酯基的取代位置多在C-4 (C<sub>18</sub>类)和C-18 (牛扁碱型)上, 仅少数在C-14或C-8/C-14上。结合植物中的分布, 考虑多数酯基取代的位置似乎以C-14 C-18 C-8 C-8/C-14的方向而变化。

## 2.3 氧化程度和位置

氧化程度常以氧取代基(羟基、甲氧基、酯基等)的多寡来判断, 取代基愈多, 其氧化程度愈高, 也愈进化。就分类学价值来说, 氧化程度和位置对C<sub>18</sub>-和C<sub>19</sub>-二萜生物碱要比C<sub>20</sub>-二萜生物碱更具价值些。在C<sub>18</sub>-和C<sub>19</sub>-二萜生物碱中, 最常见甚至共同的取代位置是C-1、C-8、C-14和C-16上。然后, 再由C-3、C-13 C-3/C-13 C-15 C-3、C-13、C-15或C-3、C-10、C-13、C-15的顺序而高级化。应当指出的是, 15-羟基者如15-羟基尼奥灵(15-hydroxylneoline)和附子灵(fuzziline)等往往也是进化的结构特征。

## 2.4 14-氧取代基

在C<sub>18</sub>-和C<sub>19</sub>-二萜生物碱中, 乌头碱型多具14-羟基或酯基, 而牛扁碱型则绝大多数为14-甲氧基取代。若再结合它们在植物中的分布, 是可以提供有用的分类信息的。

## 2.5 甲氧基

几乎所有C<sub>18</sub>-和C<sub>19</sub>-二萜生物碱中都含有甲氧基。而C<sub>20</sub>-二萜生物碱中，除极个别化合物如凉宁碱(liangshanine)、黄乌宁碱(vilmorinianine)和双二萜生物碱等外，其余均不含有甲氧基。所以，甲氧基也可作为植物化学分类的特征性结构指标。

## 2.6 7,8-次甲二氧(OCH<sub>2</sub>O)基

初步统计，除刻利定(kiridine)(从*A. kirinense* Nakai中分离出)外，含7,8-次甲二氧基的二萜生物碱仅仅限于牛扁碱型C<sub>19</sub>-二萜生物碱中，且全部分布于翠雀属植物中。这是非常特征的植物化学分类指标，应该具有重要的价值。

综上所述，二萜生物碱的结构类型对于属和亚属以及某些系(如甘青鸟头系等)的分类有重要价值。而其他化学指标如酯化程度和位置等，则可在亚属下系的划分中提供十分有用的信息。

## 3 二萜生物碱的生源关系及其分类学意义

### 3.1 生源关系

现代生物合成研究表明，牻牛儿基牻牛儿焦磷酸酯(GGPP)环合成*ent*-copaly diphosphate后经一系列步骤生物合成成为二萜阿替烷类(atisanes)和考烷类(kauranes)(MacMillan & Beale, 1999)(图2)。它们分别再通过氨基化(Wang & Liang, 2002)生成阿替生型(如atisine等)和维特钦型(如veatchine等)C<sub>20</sub>-二萜生物碱，由此再生成各种不同类型的生物碱(图3)。Ichinohe(1978)首次系统提出二萜生物碱的生源关系，且它的许多观点都被后来的大量研究事实所佐证。后来，郝小江等(1985)在此基础上，也讨论了二萜生物碱的生源关系，不足之处是过于简化以及提出纳哌啉型唯一源于维特钦型而不包括光翠雀

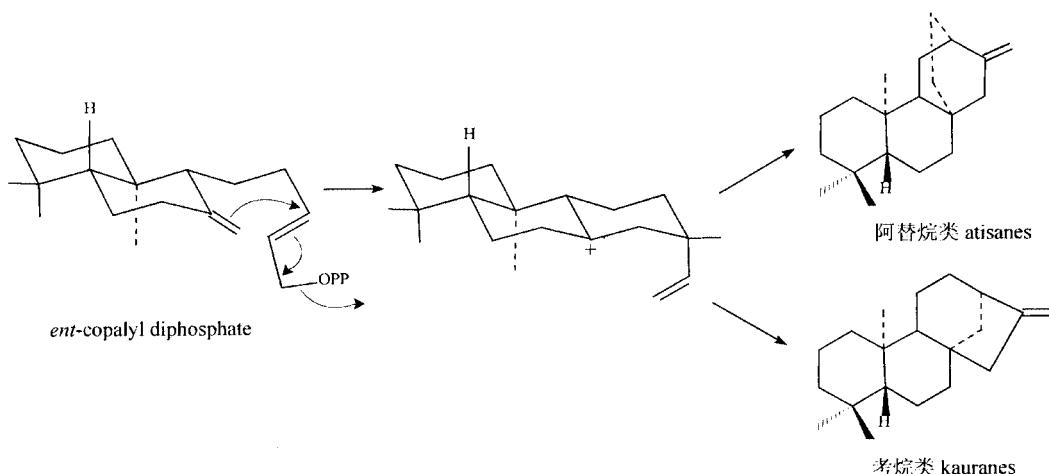


Fig. 2. Biosynthesis pathway of atisane- and kaurane-type diterpenes.

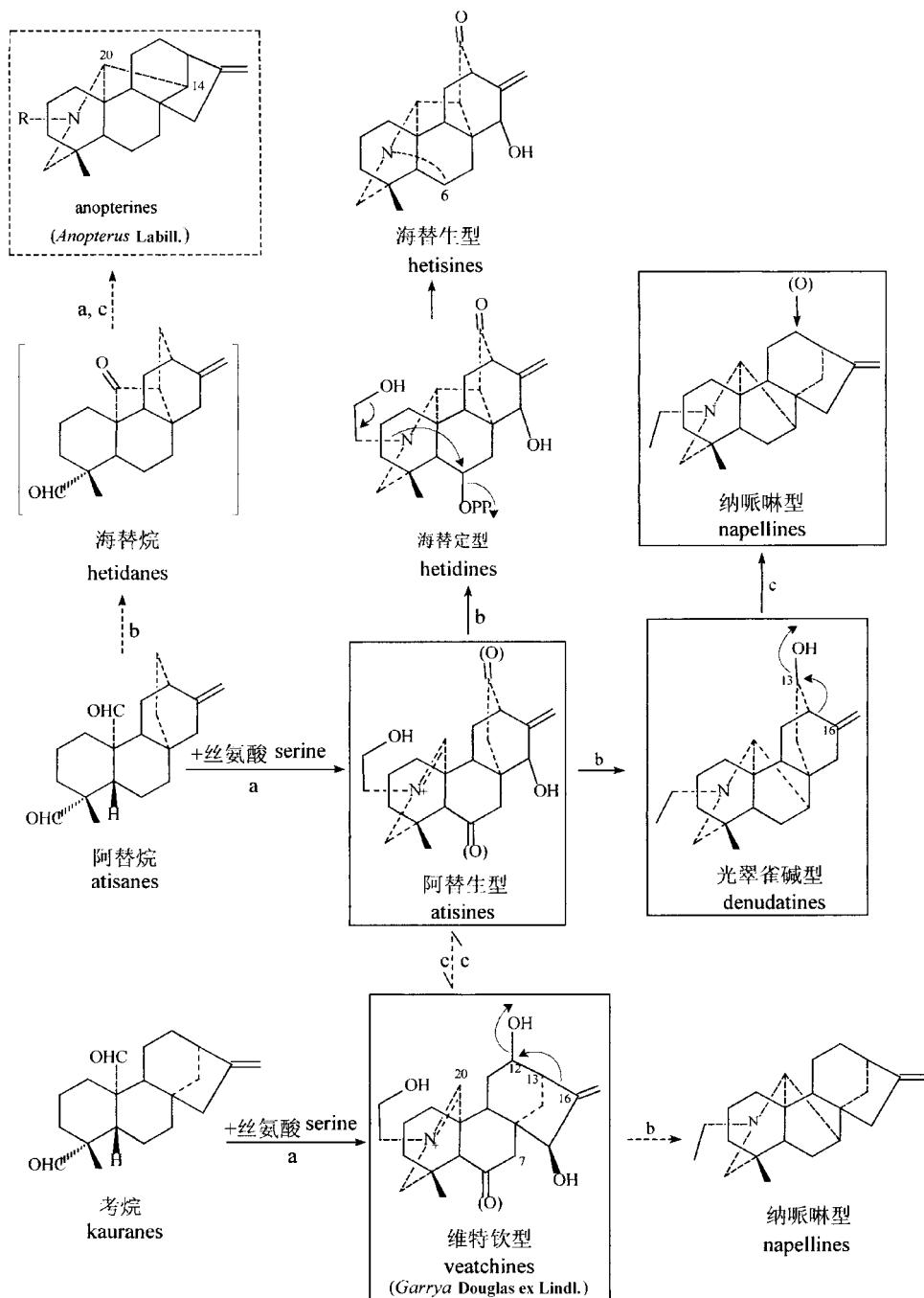
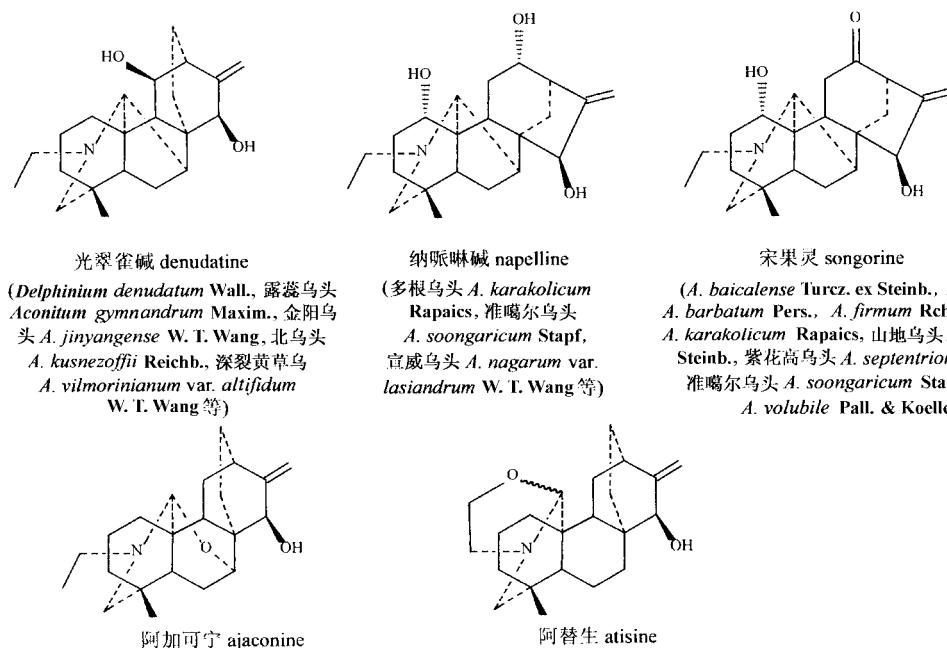


图3 C<sub>20</sub>-二萜生物碱之间的生源关系 实黑框线示关键的生源化合物, 虚黑框线示可能的生源化合物。a, 氨基化; b, Mannich反应; c, Wagner-Meerwein重排。

Fig. 3. A plausible biogenetic relationship between the C<sub>20</sub>-diterpenoid alkaloids. Here and elsewhere in this paper, the bold square line indicates the key biogenetic compounds and the dotted square line indicates the possible key biogenetic compounds. a, amination; b, Mannich reaction; c, Wagner-Meerwein rearrangement.

碱型的假设值得商榷。更何况至今未从乌头属和翠雀属植物中分出维特钦型二萜生物碱。此类碱仅仅分布于 *Garrya* 属植物中。Sultankhudzhaev 和 Nishanova (1995) 在化学、生化和假设的基础上, 也提出了二萜生物碱的模式生源关系。不足之处也是过于简化。Wang 和 Liang (2002) 对 C<sub>20</sub>-二萜生物碱的生源从化学上也进行了归纳总结。同年, Ichinohe (2002) 和 Ichinohe 等 (2002) 再次从植物化学分类的角度补充了原乌头宁碱型、原牛扁碱型以及高乌宁碱型和冉乌宁碱型内容, 我们同意这些补充。不足的是他放弃了由纳哌啉型生物合成乌头碱型二萜生物碱的途径, 并继续忽视了阿加可宁 (ajaconine) 在牛扁碱型二萜生物碱形成中的特殊作用。仔细分析上述不同假设, 我们提出二萜生物碱的生源关系如图 3-5 所示。

由图 3 可以看出: (1) 在由二萜到阿替生型二萜生物碱的生物转化中, 阿替烷可能是唯一的前体二萜化合物, 而阿替生型则在光翠雀碱型、纳哌啉碱型、海替定型和海替生型以及可能的维特钦型生物合成中处于核心地位。(2) 考虑到维特钦型至今仅仅分布于 *Garrya* 属植物中, 所以, 提出主要由考烷二萜形成的观点, 而阿替生型 维特钦型 纳哌啉型途径则处于次要地位。(3) 阿诺特啉型仅分布于 *Anopterus* 属植物中, 所以, 它应经可能的海替烷独立成一个生源分支。



由图 4 可归纳出: (1) 由阿替生、光翠雀碱和纳哌啉 3 个途径完成从 C<sub>20</sub>-二萜生物碱到乌头碱型 C<sub>19</sub>-二萜生物碱的生物转化。这与 Ichinohe (1978) 的观点相同。但在原乌头宁碱型 (Ichinohe, 2002; Ichinohe et al., 2002) 形成之前, 是经过了关键中间体重排的 C<sub>20</sub>-二萜生物碱 A、B 和 C 的。(2) 由于光翠雀碱 (denudatine) (I 型) 和纳哌啉碱 (napelline) (VII 型), 尤其是宋果灵 (songorine) (XII 型) 在乌头属植物中广泛分布 (Wang & Liang, 2002), 故可以推断光翠雀碱和纳哌啉途径是乌头碱型二萜生物碱形成的主要途径 (图 4 中粗线示), 阿替生途

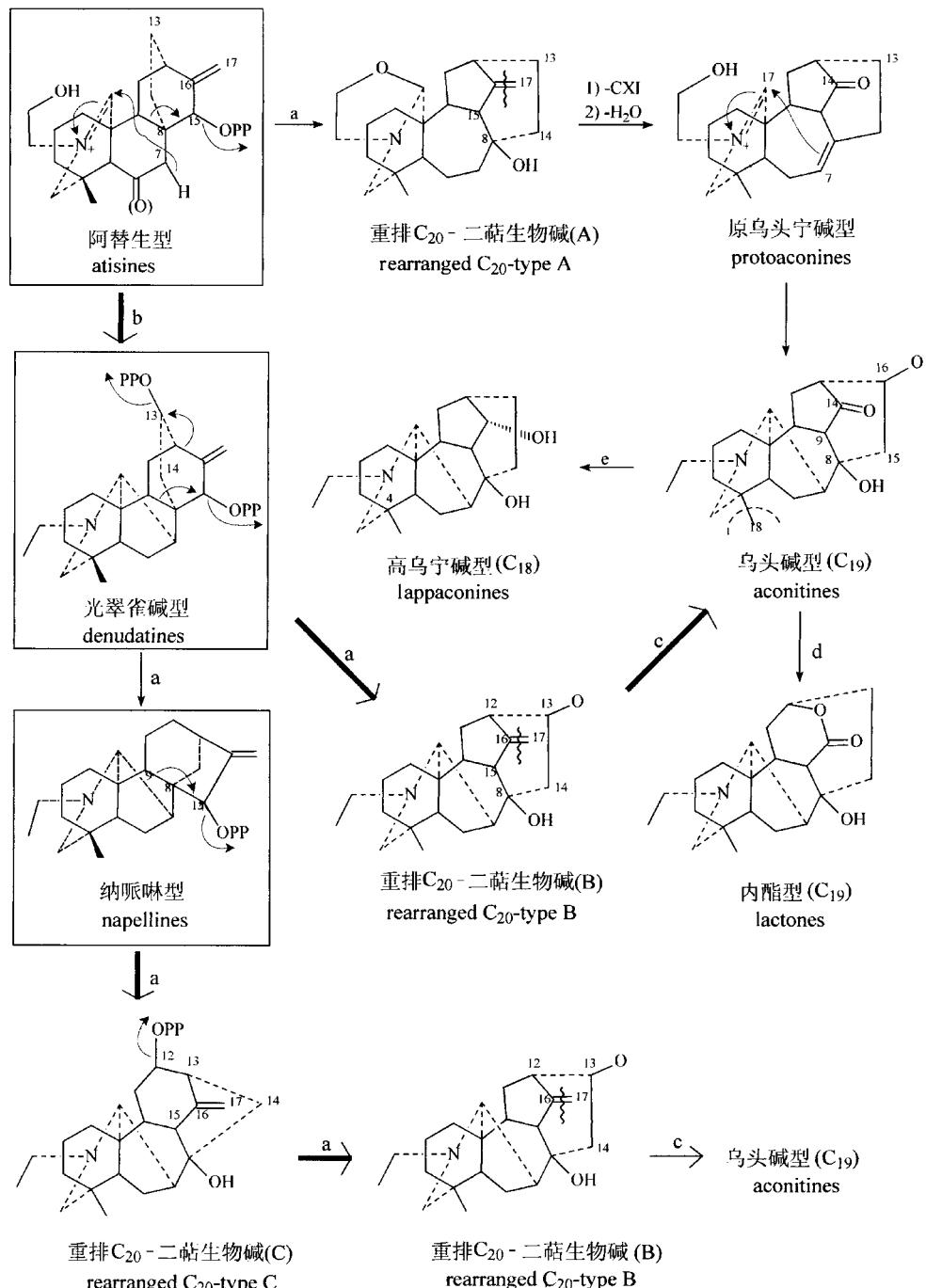


图4 阿替生型、光翠雀碱型、纳哌啉型和乌头碱型二萜生物碱之间的生源关系 a, Wagner-Meerwein重排; b, Mannich反应; c, 烯氧化裂解; d, Baeyer-Villiger氧化; e, 氧化降解失1个碳原子。

**Fig. 4.** A plausible biogenetic relationships between atisines, denudatiens, napellines, aconitines, and lappaconines. a, Wagner-Meerwein rearrangement; b, Mannich reaction; c, oxidative cleavage of olefine; d, Baeyer-Villiger oxidation; e, loss of one carbon via oxidation.

径则可能处于次要地位。

Ichinohe(1978)提出的阿替生型 牛扁碱型的生源途径比较含糊。2002年该作者(Ichinohe, 2002; Ichinohe et al., 2002)又补充了经原乌头宁碱型形成牛扁碱型的新观点。我们认为赞成这种假设。此外, 考虑到牛扁碱型主要分布于翠雀属植物中, 特别是阿加可宁(ajaconine)(VII型)广泛分布于该属植物(迄今未从乌头属分出)的事实, 我们认为阿加可宁很可能是翠雀属植物中牛扁碱型二萜生物碱的最重要的前体物(阿加可宁途径)(图5)。同样地, 由C<sub>20</sub>-二萜生物碱到C<sub>19</sub>-二萜生物碱必须经过关键中间体重排的C<sub>20</sub>-二萜生物碱A和B'(图5)。另外, 由图3-5也不难理解为什么绝大多数C<sub>18</sub>-和C<sub>19</sub>-二萜生物碱都具C-7、C-8、C-14和C-16氧取代基的原因, 以及阿替生、光翠雀碱和纳哌琳碱中15-羟基在骨架生物转化中的重要作用。

### 3.2 分类学意义

**3.2.1** 在氨基化后二萜生物碱的骨架形成与演化关系, 本质上就是在植物体内酶的催化下所进行的C-C键的形成、增减与迁移。其分类学价值就在于进化程度的比较, 其顺序依C<sub>20</sub><C<sub>19</sub><C<sub>18</sub>依次递增。所以, 可以认为若植物类群中C<sub>20</sub>类分布愈多, 则该类群愈原始, 如准噶尔乌头系中主成分为C<sub>20</sub>类光翠雀碱等。与此相反, 若植物中C<sub>19</sub>类分布愈多, 或以此为主成分, 而C<sub>20</sub>类次之或分散分布, 如乌头系和蔓乌头系等, 则表明该植物类群愈进化。

但应强调指出的是, 上述比较, 似乎只有在同一类群植物中进行才有意义。例如, 许多证据说明牛扁亚属植物要比乌头亚属植物原始。可是, 几乎所有的C<sub>18</sub>-二萜生物碱都存在于牛扁亚属植物中。若由此推断牛扁亚属要比乌头亚属更进化, 显然有失偏颇。只可以说在牛扁亚属植物类群中, 与C<sub>19</sub>-二萜生物碱比较, C<sub>18</sub>-二萜生物碱多的或为主体成分者可能较为进化。

此外, C<sub>20</sub>-二萜生物碱类如阿替生、阿加可宁、光翠雀碱、纳哌琳碱和宋果灵等是形成乌头属、翠雀属和飞燕草属等植物中二萜生物碱的最重要的前体物。

**3.2.2** 染色体证据表明, 翠雀属的核型不对称性明显高于乌头属, 从而说明翠雀属要比乌头属更进化(杨亲二, 2001)。研究还表明, 乌头属和翠雀属形成姐妹群关系, 而二者与飞燕草属的关系则较远(罗艳, 2003)。但是, 若仅仅比较二萜生物碱的分布, 似乎翠雀属(酯化程度低, 且多取代在C-18上)与牛扁亚属的进化程度相当。但是, 若再考虑在翠雀属中复杂的双二萜生物碱和具有7,8-次甲二氧基牛扁碱类的存在、C<sub>20</sub>类分布较少的特点以及这两个属存在的平行演化趋势(王文采, 1979; 李良千, 1998; 杨亲二, 1996, 2001), 似乎就能支持翠雀属比乌头属更进化的观点。所以, 植物化学分类既要比较分析化学成分, 又要综合考虑化学成分在同一类群的分布以及平行演化等方面的因素。

**3.2.3** 与大多数植物成分的生物合成相类似, 二萜生物碱骨架类型形成后的官能化(羟基化、甲氧基化、酯化等)是其种类增加和复杂化的主要原因, 而官能化之前最常见而原始的关键前体物胺醇类二萜生物碱则对于判断演化程度或次序, 常能提供有用的信息。现以国产乌头属植物中乌头碱型二萜生物碱为例, 来说明二萜生物碱形成中的关键前体胺醇物及其可能的演化关系(图6)。

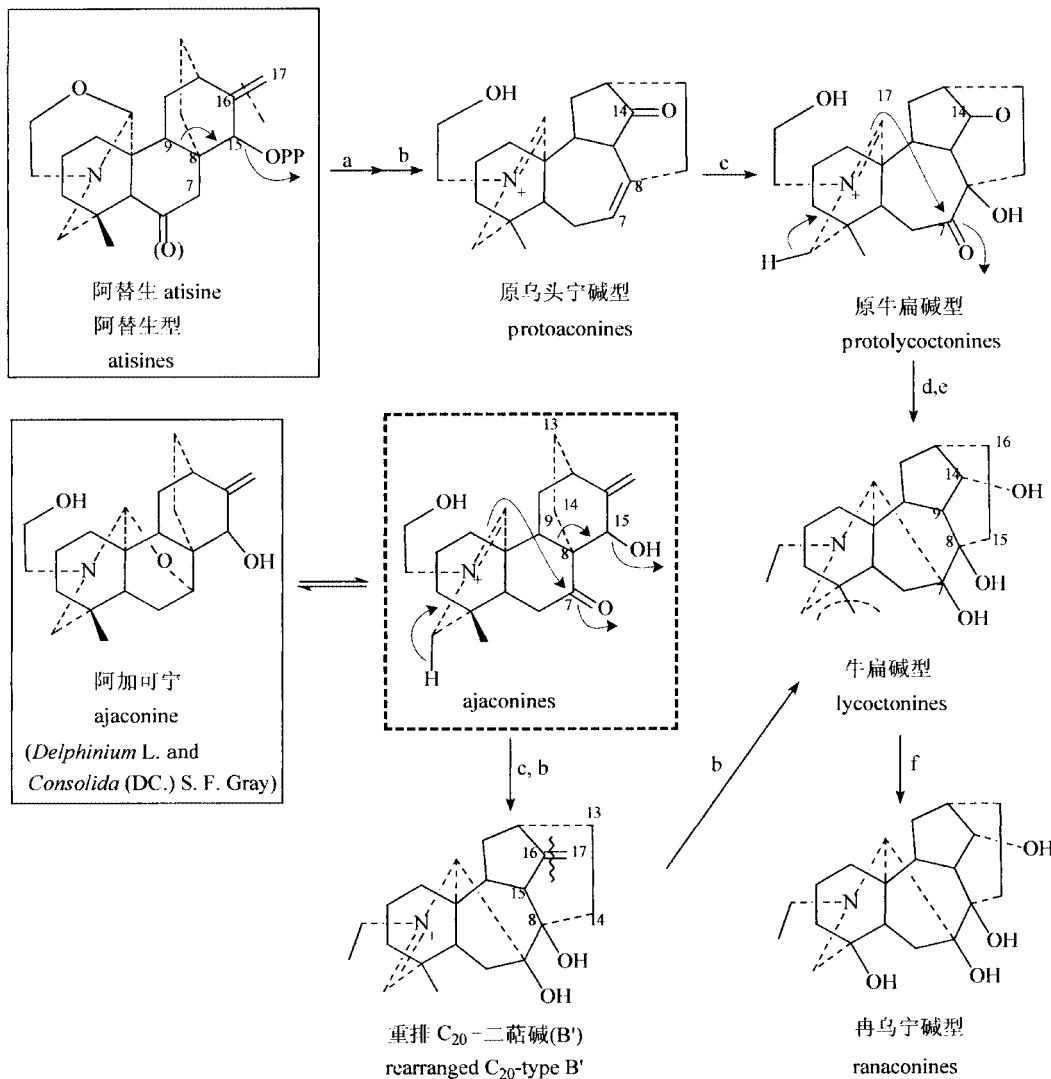
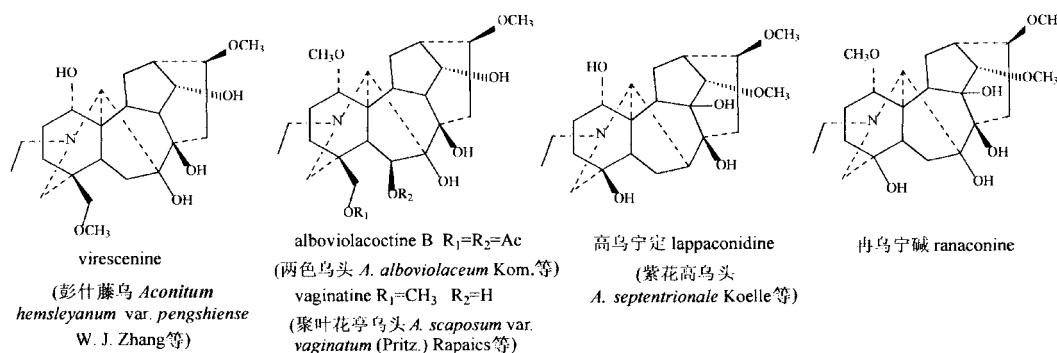


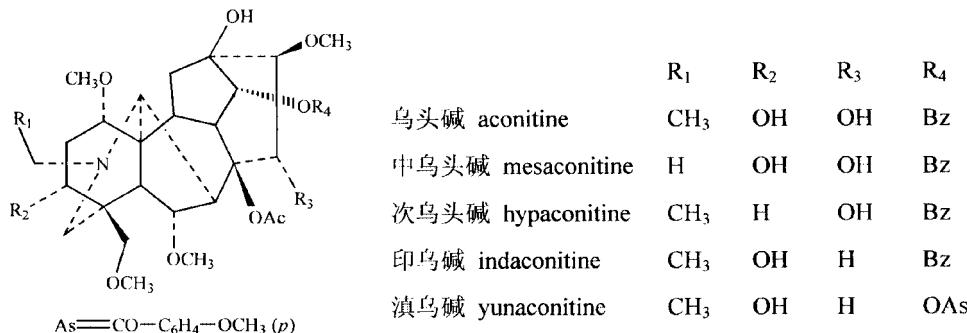
图5 阿替生型C<sub>20</sub>-二萜碱与牛扁碱型(C<sub>19</sub>)和冉乌宁碱型(C<sub>18</sub>)二萜碱之间的生源关系 a, Wagner-Meerwein重排; b, 烯氧化裂解; c, 烯双羟化-氧化; d, 酮醛缩合; e, 亚胺盐还原; f, 氧化降解失1个碳原子。

Fig. 5. A newly proposed biogenetic relationship between atisine ( $C_{20}$ ), lycocotonines ( $C_{19}$ ), and rananconines ( $C_{18}$ ). a, Wagner-Meerwein rearrangement; b, oxidative cleavage of olefin; c, olegamic dihydroxylation-oxidation; d, aldol condensation; e, reduction of iminium salt; f, loss of one carbon via oxidation.

由图6不难理解, 塔拉萨敏、尼奥灵和查斯曼宁广泛分布的原因是因为它们处于关键中间体的位置。同样, 牛扁碱型二萜生物碱的官能化中, 广泛分布的牛扁碱是一个关键中间体, 而其来源可能与维利森尼(virescenine)、阿保维亭乙素(alboviolacocetine B)或瓦其那亭(vaginatine)等有关。C<sub>18</sub>-二萜生物碱中, 胺醇物高乌宁定和冉乌宁碱既是类型的代表, 又可视为官能化的关键前体物。



3.2.4 根据愈复杂愈比较进化的原则, 可以列出乌头属植物中分布比较多的高度进化的乌头碱型的二萜生物碱有: 乌头碱(aconitine)、中乌头碱(mesaconitine)和次乌头碱(hypaconitine)等。此外, 滇乌碱(yunaconitine)、印乌碱(indaconitine)等也是比较进化而广泛分布的此类生物碱。这些生物碱反映了官能化的最高程度, 而且也间接说明了所在植物类群的进化性, 在亚属以下划分中具有重要意义。



以上分析充分地说明了二萜生物碱的生源关系与其在植物中的分布以及植物化学分类密切相关。

#### 4 药效和毒性

乌头属植物在我国供药用者已达76种之多。著名的有附子、北乌头、雪上一支蒿、关白附、榜嘎(藏医名, *A. naviculare* (Brühl.) Stapf)等。本属传统疗效指数(肖培根等, 1986)为祛风除湿(5582)、活血祛瘀(499)、温里散寒(313); 用于治跌打损伤(4489)、关节炎(6458)、神经性疼痛(433)、中风瘫痪(1230)、胃冷痛(400)、胃肠炎(582)、月经不调(320)、痈疽疮毒(2701)等。现代药理研究表明, 乌头属植物或其生物碱在镇痛、抗炎、抗心律不齐和强心作用等方面始终受到国际上的关注, 并已有刺乌头碱(lappaconitine)、3-乙酰乌头碱(3-acetylaconitine)等作为药品生产。本属植物常具有强烈毒性, 毒副作用便成为新药开发的关键。表5是一些有代表性乌头生物碱的毒性情况。

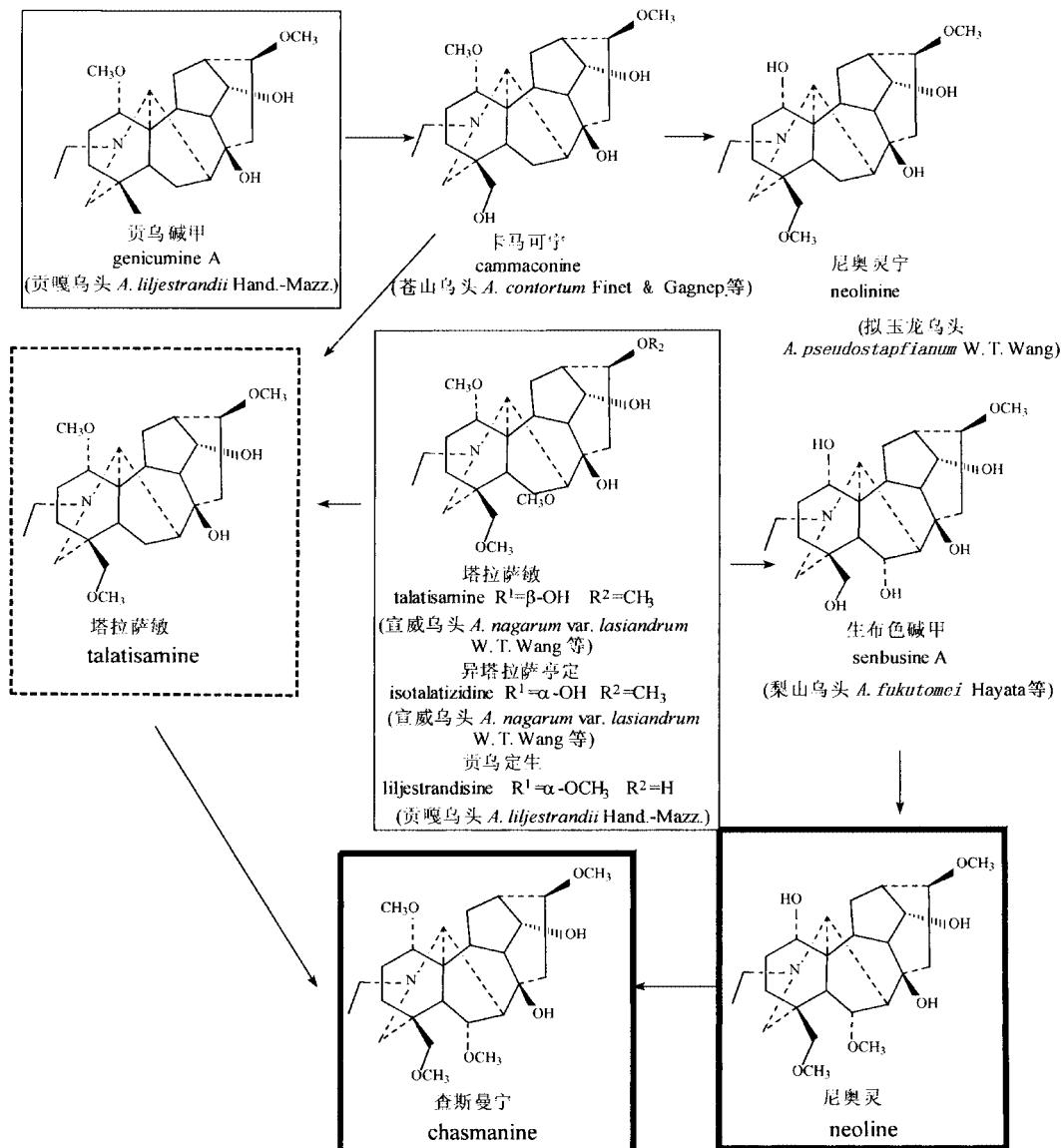


图6 中国乌头属植物中二萜生物碱生源上可能的关键前体及其演化关系(粗黑框示广泛分布的关键生源化合物)

Fig. 6. The plausible key biogenetic precursors of diterpenoid alkaloids of *Aconitum* from China (The thick square line indicates the widely distributed key biogenetic compounds).

## 5 国产乌头属植物的药用亲缘学的讨论

### 5.1 牛扁亚属

已有16种做了化学研究。该亚属由几乎全部的C<sub>18</sub>-二萜生物碱(I、II)和牛扁碱型(IV)为主的C<sub>19</sub>-二萜生物碱组成特征性化学成分。除极少数如查斯曼宁、沙可宁(saconine)

表5 二萜生物碱对小鼠的急性毒性(LD<sub>50</sub> mg/kg)Table 5 Toxicities of diterpenoid alkaloids on mice(LD<sub>50</sub> mg/kg)

生物碱 Alkaloid	给药途径 Administration			
	口服(po)	皮下(im)	腹腔(ip)	静脉(iv)
乌头碱 aconitine	1.8	0.29–0.31	0.30–0.38	0.12–0.27
中乌碱 mesaconitine	1.8	0.20–0.26	0.2–0.3	0.10–0.13
次乌碱 hypaconitine	5.8	1.19	1.10	0.47
印乌碱 indaconitine				0.47
滇乌碱 yunaconitine	2.97	0.37	0.340–0.585	
北乌碱 beiwutine		0.39		0.42
3-乙酰乌头碱 3-acetylaconitine	2.5	0.58–1.00	0.71	0.47
苯甲酰乌头碱 benzoylaconitine			70	23
苯甲酰中乌头碱 benzoylmesaconitine	830	230	240	21
苯甲酰次乌头碱 benzoylhypaconitine	810	130	120	23
乌头原碱 aconine				116–120
塔拉萨敏 talatisamine				115
尼奥林 neoline		7400		
高乌碱 lappaconitine		11.7	10.5	11.5
冉乌碱 ranaconitine		9.0		
雪乌碱 penduline		3.9		
关附甲素 Guan-Fu base A			421	134
关附庚素 Guan-Fu base G			185.5	
关附辛素 Guan-Fu base H				33.7
光翠雀碱 denudatine		207		
阿替生 atisine				9.0
海替生 hetisine				26.0
宋果灵 songorine			480	142.5
异叶乌头碱 heteratine				192

等比较原始的胺醇外，尚无更复杂的乌头碱型二萜生物碱发现，而C<sub>20</sub>-二萜生物碱则零散分布。所有这些都说明牛扁亚属是一个演化水平相对比较原始的类群。这与形态学(多年生根状茎)(王文采, 1979)的证据相一致。植物化学分类上，郝小江等(1985)以为牛扁亚属为含牛扁碱型生物碱的类群，我们基本同意这种提法，但需补充为牛扁亚属是以含牛扁碱型和C<sub>18</sub>-二萜生物碱为主的类群。

## 5.2 乌头亚属

该亚属是国产乌头属中最大最复杂的一个类群。牛扁亚属具多年生根状茎，乌头亚属则具二年生块根。细胞学上，横断山区的牛扁亚属植物大多为多倍体，同一产区的乌头亚属则多为二倍体(罗艳, 2003)。这从细胞学上说明乌头亚属可能要比牛扁亚属进化。分子系统学证据表明，我国华北、东北产的乌头亚属与欧洲、北美及日本乌头亚属植物较为相近，但形态上却显著不同于横断山区的种类，而遗传差异却很小(罗艳, 2003; Luo et al., 2005)。按照王文采(1979)的分类系统，国产乌头亚属分为多果乌头组和乌头组。前者仅一种多果乌头*A. polycarpum* Chang ex W. T. Wang, 未见化学成分研究。后者分为11个系。核基因组内转录间隔区(ITS)的系统树表明：多果乌头确实可与别的乌头亚属植物明显分开，而且岩乌头和褐紫乌头也各自成为一个独立分支与其他乌头亚属植物分开；其余乌头亚属植物在ITS系统树中明显聚成二支：一支包括了唐古特乌头系、圆叶乌头系、保山乌头系及短柄乌头系(形态上与种子光滑、无横膜翅、花瓣分化不完全、距不发达相对应)，

另一支则包括了乌头系、兴安乌头系、显柱乌头系、蔓乌头系，并完全打破了彼此之间的界限而与准噶尔乌头系聚成一支(种子一面生有横膜翅，花瓣分化较完全)。为了讨论方便我们仍以王文采乌头亚属下9个系的系统为基础，并结合罗艳(2003)和Luo等(2005)的最新研究成果进行讨论。

**5.2.1 唐古特乌头系和圆叶乌头系** 唐古特乌头系中仅甘青乌头有化学成分报道。圆叶乌头系也仅圆叶乌头和美丽乌头进行了化学研究。3种植物的化学研究都不够充分。两个系中主要存在内酯型和散在分布的C<sub>20</sub>-二萜生物碱。内酯型二萜生物碱至今未从其他植物类群中分出。所以，可以认为内酯型二萜生物碱是甘青乌头系和圆叶乌头系的特征性化学分类指标。植物化学分类上可将此二系称为内酯型二萜生物碱类群。这两个系从形态上(王文采, 1979)和化学上(郝小江等, 1985)均显示出原始类群的特征，我们同意此种看法。这也与生源上内酯型二萜生物碱是C<sub>20</sub>-C<sub>19</sub>类转化的早期阶段经重排的C<sub>20</sub>-型中间体(A、B、B')形成的假设相符合(图4, 5)。此类群植物的毒性在乌头属中最小，显示作为新药开发的前景也最大。

**5.2.2 保山乌头系** 该系包括5个类群(小白撑、无距小白撑、宣威乌头、宾川乌头和雷波乌头)进行了化学研究，其中对宣威乌头的研究比较深入。该系的这些种的化学成分除以主成分存在的光翠雀碱型如光翠雀碱等和较多的纳哌啉碱型如宋果灵等C<sub>20</sub>-二萜生物碱外，尚共存有高度进化的乌头碱型如乌头碱、去氧乌头碱等和较进化的含14-大茴香酸酯基的乌头碱型如滇乌碱、黄草乌碱甲(vilmorrianine A)等以及较原始的乌头碱型胺醇如塔拉萨亭定和尼奥灵等，充分显示出中间过渡类群的特征。所以，保山乌头系可称为以C<sub>20</sub>-二萜生物碱如光翠雀碱和宋果灵以及C<sub>19</sub>-二萜生物碱如乌头碱、滇乌碱、塔拉萨亭定和尼奥灵等为主的典型的中间过渡类群。

**5.2.3 短柄乌头系** 除拟黄花乌头外，该系中有些种类已进行了充分的化学研究，如多裂乌头、伏毛铁棒锤、铁棒锤和黄花乌头。其中前3种化学成分显示出以3-乙酰乌头碱、乌头碱、伏乌碱(flavaconidine)等高度进化的乌头碱型二萜生物碱为主，胺醇如尼奥灵次之，有时共存纳哌啉型C<sub>20</sub>-二萜生物碱的特征。据此，似乎该系与高度进化的乌头系相近。根据化学成分、毒性以及根部组织形态(李鸣等, 1991)，黄花乌头与本系中其他成员均有十分显著的差异，似乎将其从本系分出，与拟黄花乌头另成立一个独立的系更为合理。

**5.2.4 显柱乌头系** 该系共有12种植物进行了化学研究(表3)。唯其中普格乌头和亚东乌头研究甚少。除苍山乌头外，该系的化学特征是：既有酯化程度高的双酯类二萜生物碱，又有较原始的胺醇类如genicunine A、塔那萨敏和查斯曼宁等。单酯或双酯类中，芳香酯基有大茴香酸酯基和苯甲酸酯基之分，且多数为14-大茴香酸酯基，如滇乌碱、草乌甲素(crassicauline A)、黄草乌碱甲和滇南碱(austraconitine)等。其中滇乌碱几乎成为共同存在的成分。该系是含大茴香酸酯基的二萜生物碱最为集中分布的植物类群。此外，该系未见尼奥灵和C<sub>20</sub>-二萜生物碱，则是表明其比保山乌头系更进化的证据；而无15-氧取代(羟基等)的乌头碱型二萜生物碱的存在，则又证明该系演化程度上不如蔓乌头系和乌头系。另外，苍山乌头是一个比较特殊的植物。其化学成分主要以海替定型C<sub>20</sub>-二萜生物碱如紫乌定(episcopalidine)等和冉乌宁碱型C<sub>18</sub>-二萜生物碱为主(王锋鹏, 方起程, 1983；杨亲二,

1990; Niitsu et al., 1992)。前者是原始的特征, 后者则较进化。更有趣的是, 至今未从苍山乌头中分出含大茴香酸酯基的二萜生物碱, 所以该种的分类位置值得再研究。

综上所述, 显柱乌头系可视为以含大茴香酸酯基的乌头碱型二萜生物碱以及塔拉萨敏和查斯曼宁胺醇类为主的类群。

**5.2.5 兴安乌头系** 已对该系中的8种植物进行了比较充分的化学研究。其化学成分特征与显柱乌头系颇为相似, 即均以含大茴香酸酯基的乌头碱型和较原始的胺醇为主。稍差异之处是个别植物如展花乌头有尼奥灵甚至印乌碱等出现, 而化学研究不充分的马耳山乌头则与苍山乌头十分相似, 即都以C<sub>18</sub>-二萜生物碱为主。更有价值的是从马耳山乌头中分出特征性成分滇乌碱。所以, 也可认为兴安乌头系是以含大茴香酸酯基的乌头碱型二萜生物碱和塔拉萨敏和尼奥灵胺醇类二萜生物碱为主的类群, 与显柱乌头系最为相近。

**5.2.6 蔓乌头系** 该系是乌头亚属中化学成分研究比较充分的类群之一(表3)。其化学成分特征是既有酯化程度高的双酯二萜生物碱类, 又有类似于显柱乌头系和兴安乌头系所具有的胺醇类如塔拉萨敏、尼奥灵等。初步统计表明, 在含芳香酯基类二萜生物碱的植物中, 具大茴香酸酯基者与苯甲酸酯基者大体相当。这也许是蔓乌头系有别于显柱乌头系和兴安乌头系之处, 而且其化学成分的多样性, 旁证了其独立为系的可疑性。更重要的是, 本系有些植物如拟玉龙乌头和蔓乌头等已出现高度进化的含15-羟基的乌头碱型二萜生物碱, 如乌头碱、中乌头碱、去氧乌头碱和15-羟基尼奥灵等, 从而显示出与乌头系相近。所以, 可以认为该系可能是连接显柱乌头系/兴安乌头系和乌头系的中间过渡类群。

瓜叶乌头是国产乌头属植物中分布较广、极为多型的一个种, 对认识乌头属植物性状变异规律及属内的分化和演化可能有重要价值(罗艳, 2003)。杨亲二(1999)将许多变种进行了归并。迄今, 已知进行了化学研究的仅仅4个变种: 原变种瓜叶乌头、白花瓜叶乌头、拳距瓜叶乌头和彭什藤乌。比较充分的化学研究表明, 这4个变种在化学成分上存在着明显的差异。瓜叶乌头以含14-苯甲酸酯基乌头碱型二萜生物碱为主。白花瓜叶乌头则以含14-苯甲酸酯基(如乌头碱等)和肉桂酸酯基[如8-去乙酰基潘乌碱(8-deacetylsuntpaconitine)等]乌头碱型以及7,17-次裂型二萜生物碱(如大渡乌碱(franchetine)、leaeandine等)为主。彭什藤乌的化学成分似乎又介于二者之间, 即14-苯甲酸酯基(如印乌碱等)/肉桂酸酯基(如8-deacetylsungpaconitine等)乌头碱型和7,17-次裂型(如14-debenzoylfranchetine等)二萜生物碱兼而有之。拳距瓜叶乌头则更为特殊, 以含14-大茴香酸酯基的乌头碱型二萜生物碱成分为主。其中滇乌碱、草乌甲素等为双酯类。单酯中有以主成分存在的5-羟基-14-大茴香酸酯基的乌头碱型二萜生物碱, 如拳乌定(hemsleyadine)、拳乌生(hemsleyasine)和异拳乌定(isohemsleyadine)及其胺醇物。它们的结构被作者之一(Xu et al., 1996a, b; Xu & Wang, 1997)最初误定7-羟基的牛扁碱型, 近经单晶X射线分析纠正为含5β-羟基的乌头碱型二萜生物碱(Gao & Wang, 2005)。综上所述, 本种在化学上存在较大的变异, 似乎应慎重对待瓜叶乌头变种的合并。

**5.2.7 乌头系** 该系有10种植物做了化学研究。其中除大苞乌头和锐裂乌头外, 其余种类的化学研究都比较充分。该系化学成分上无论是酯化程度和取代位置, 还是氧化程度和位置上都呈现高度进化的特征。该系是以含15-羟基的单酯或双(多)酯或胺醇的乌头碱

型二萜生物碱为特征性主成分。代表性生物碱如乌头碱、3-乙酰乌头碱、中乌头碱、次乌头碱、介沙乌头碱(jesaconitine)、去氧乌头碱、北乌碱(beiwutine)、附子灵(fuziline)、15-羟基尼奥灵、senbusine B和C等。应注意的是,研究充分的北乌头除了“残存分布”的少数C<sub>20</sub>-二萜生物碱如北乌亭(beiwutine)和北乌定(beiwudine)外,还具有含5-羟基的isohemsleyanidine及其胺醇物hemsleyanidine,显示出与蔓乌头系相近的演化关系。

**5.2.8 准噶尔乌头系** 对该系已报道的5种植物准噶尔乌头、多根乌头、展毛多根乌头、伊犁乌头和林地乌头的化学成分分析,显示该系的化学特征类似于保山乌头系。它是以高度进化的乌头碱型如10-羟基乌头碱(aconifine)、乌头碱、去氧乌头碱等和比较原始的胺醇如塔拉萨敏、尼奥灵等以及C<sub>20</sub>-二萜生物碱如宋果灵等为主的植物类群。化学特征似乎显示该系更靠近保山乌头系。

**5.2.9 岩乌头系** 这是一个形态和生存环境都很特殊的植物类群。仅对一种植物彭州藤乌做了比较深入的化学研究。其化学成分比较原始,以牛扁碱型和乌头碱型的胺醇二萜生物碱如牛扁碱、维生尼碱(verescenine)和异塔拉亭定以及C<sub>20</sub>-二萜生物碱为主,其中包括新骨架类型的彭乌生碱(racemulosine)。所有这些都显示岩乌头系是一支比较原始而又特殊的类群,值得进一步研究。

**5.2.10 褐紫乌头系** 该系化学研究较少,仅两种植物金阳乌头和褐紫乌头有化学成分报道。其化学特征是以C<sub>20</sub>-二萜生物碱如光翠雀碱和宋果灵等为主,其次尚有高度进化的乌头碱型生物碱如乌头碱等成分。该系系统演化水平似乎介于保山乌头系和短柄乌头系之间。化学分类似不支持将其独立成一个分支。

根据植物化学分类的初步研究,总结乌头亚属内系统之间关系是:唐古特乌头系、圆叶乌头系、保山乌头系、短柄乌头系、准噶尔乌头系和褐紫乌头系可能代表该亚属的原始类群。其中唐古特乌头系与圆叶乌头系相似;将褐紫乌头系独立成一个分支,化学分类证据似不支持,它可能是连接保山乌头系和短柄乌头系的“桥梁”。准噶尔乌头系则更靠近保山乌头系。显柱乌头系、兴安乌头系、蔓乌头系和乌头系代表进化类群。其中显柱乌头系与兴安乌头系相似。蔓乌头系植物表现出化学成分上的多样性,呈现出与乌头系的密切联系。岩乌头系独立成一个分支,可能较为原始。保山乌头系可能是其他系的原始前体类群。

### 5.3 露蕊乌头亚属

该亚属形态上比较特殊。有些学者认为它与乌头亚属关系较近(解剖学:李鸣等,1991;细胞学:商效民,李正理,1984;商效民,1985;植物化学:肖培根等,1984;郝小江等,1985)。但是,分子系统学(罗艳,2003)又不支持这一观点。其系统位置也不确定。从习性(Tamura, 1966;王文采,1979)和种子结构(杨亲二,1990)性状来看,它比乌头亚属更进化。可是,染色体(商效民,1985)、根部组织构造(李鸣,冯毓秀,1990)、植物化学(肖培根等,1984)对此不予支持。其中可能的原因是不同性状演化的速率不同(罗艳,2003)。

露蕊乌头亚属仅含一种植物露蕊乌头。其化学成分以乌头碱型胺醇类,如塔拉萨敏等及其单酯类为主,散布C<sub>20</sub>-二萜生物碱如gymnadine和阿替生盐等,显示比较原始的化学特征。综合露蕊乌头形态、植物化学、生物分子等各方面的信息,似乎将其从亚属上升为一个独立属更为合适。

## 6 结语

乌头属是被子植物中分类上十分困难的类群,至今没有一个比较完善的属下分类系统。本文总结了前人对该属的植物化学研究结果,从植物化学和药用植物亲缘学方面探讨了该属的一些系统学问题,但对本属系统客观和全面的修订则还有许多工作要做。应当指出的是,以往的一些植物化学研究结果在种类的鉴定上有时不十分可靠,从而难免会影响植物化学分类的结果。因此,我们认为在以后的研究工作中,植物化学家应加强与分类学家的合作,注意保存凭证标本,以保证样品学名鉴定的准确性,使我国的植物化学分类和药用植物亲缘学的研究提高到更高水平。

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