Progress of Picrotoxane Type Alkaloids in *Dendrobium*Jingjuan Li,^{a,b,c} Fucai Ren,^{a,b,c} and Jiangmiao Hu^{*a,b}^a State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, Yunnan 650201, China^b Yunnan Key Laboratory of Natural Medicinal Chemistry, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, Yunnan 650201, China^c School of Chemical Sciences and Technology of Yunnan University, Kunming, Yunnan 650091, China

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Abstract *Dendrobium* has a long clinical usage history and diverse chemical compositions. The picrotoxane type alkaloid represented by dendrobine from *Dendrobium* species has antipyretic and anti-hypertensive activities. Since the 1930s, the study of dendrobine has made a huge progress, including many new reported picrotoxane type alkaloid compounds. In this article, some developments of picrotoxane type alkaloids in *D. wardianum* and *D. findlayanum* are described.

Keywords *Dendrobium*, picrotoxane type alkaloid, dendrobine, wardianumine A, findlayines

Picrotoxane type alkaloids, also called dendrobine-type alkaloid, only distribute in some species of *Dendrobium*. Up to now, 27 picrotoxane type alkaloids have been reported from 8 species of *Dendrobium* (Figure 1).

Figure 1 Reported picrotoxane type alkaloids in *Dendrobium*.

The first isolation of dendrobine from *D. nobile* was done by Hideki Suzuki and in 1932, then Chen Ke-Hui also got the compound in 1935.^[1,2] The sesquiterpenoid structural skeleton of dendrobine was not elucidated until that was solved by Tadamasu Onaka *et al.* in 1964,^[3] which marked the beginning of the systematic research of picrotoxane type alkaloids. Due to antipyretic and anti-hypertensive activities of this kind alkaloid and 7 contiguous stereocenters, dendrobine has become a research hotspot for organic chemists. A series of total synthesis were published in many journals and (–)-dendrobine was synthesised by Diels-Alder reaction recently with a high stereoselectivity.^[4–15]

Dendrobine-type alkaloids mainly distributed in sect.

Dendrobium of *Dendrobium* species, however, few has been reported recently.^[16] Since a long-term chemical research focused on *Dendrobium* and analysis comparison of different species, we can now ascertain which species from *Dendrobium* contain dendrobine-type alkaloids efficiently. As a result, one dendramine, named wardianumine A, was isolated from *D. wardianum* (20 in Figure 1) by us^[17] and it provides an idea for the synthesis pathway of dendrobine. Furthermore, four novel *seco*-dendrobine-type alkaloids named findlayines A–D (Figure 1, 24–27) were isolated fortunately by us from *D. findlayanum*, and the results enriched the diversity of picrotoxane type alkaloids.^[18]

Chemical studies on four new picrotoxane type alkaloids showed that two compounds (Findlayines A and B) with a 5/6/7 tricyclic cage skeleton and two compounds (Findlayines C and D) derived by the cleavage of the C₂–C₃, which is rare in this type of alkaloid. In addition, the absolute configurations of 24–27 were confirmed by single crystal X-ray diffraction (Figure 2).^[18]

Figure 2 Chemical structures of findlayines A and C.

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