



Review article

Chemical diversity of ginseng saponins from *Panax ginseng*

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ARTICLE INFO

Article history:

Received 5 November 2014

Received in Revised form

23 December 2014

Accepted 25 December 2014

Available online 10 January 2015

Keywords:

Araliaceae
dammarane
ginsenoside
Panax ginseng
triterpene

ABSTRACT

Ginseng, a perennial plant belonging to the genus *Panax* of the Araliaceae family, is well known for its medicinal properties that help alleviate pathological symptoms, promote health, and prevent potential diseases. Among the active ingredients of ginseng are saponins, most of which are glycosides of triterpenoid aglycones. So far, numerous saponins have been reported as components of *Panax ginseng*, also known as Korean ginseng. Herein, we summarize available information about 112 saponins related to *P. ginseng*; >80 of them are isolated from raw or processed ginseng, and the others are acid/base hydrolysates, semisynthetic saponins, or metabolites.

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1. Introduction

Ginseng has been one of the most important components in a number of East Asian herbal remedies. In fact, the term ginseng, without any modifier, refers particularly to the species *Panax ginseng* Meyer or sometimes even more specifically to the root of the plant species. As the name ginseng carries authority and veneration in East Asian medicine, other plants that have some properties in common with *P. ginseng* have been allegedly called “ginseng”. Eventually, ginseng has become a blanket term that encompasses >10 species of perennial plants belonging to the genus *Panax* of the family Araliaceae [1,2]. Currently, 14 plants, including 12 species and two infraspecific taxa, have been recognized as members of the genus *Panax*, as shown in Table 1 [3]. Some of the *Panax* plants have common names, which stem from their countries of origin: *P. ginseng*, *Panax japonicus*, *Panax notoginseng*, *Panax quinquefolius*, and *Panax vietnamensis* are also called Korean ginseng, Japanese ginseng, Chinese ginseng, American ginseng, and Vietnamese ginseng, respectively. Of the *Panax* plants, Korean ginseng, Chinese ginseng, and American ginseng have been commercially cultivated; Vietnamese ginseng has recently been

introduced for agriculture. Most ginseng species are native to Asia, especially East Asia. Thus, the use of equivocal names, such as Asian ginseng that often refers to *P. ginseng*, is discouraged.

While the variety of species renders some pharmacological effects specific to certain species, ginseng, in general, displays restorative, tonic, and revitalizing properties [4]. Thus far, >6,000 articles regarding the traditional uses, chemical constituents, and biological and pharmacological effects of ginseng have been published since Petkov [5] reported the pharmacological properties of *P. ginseng* extracts in the 1950s. Such pharmacological activities of ginseng have been found to be mainly attributed to ginseng saponins, also known as ginsenosides [6–11].

Since the first isolation of six ginsenosides from *P. ginseng* in the 1960s [12], plenty of ginsenosides have been isolated and identified from the species. In this review, we recapitulate the chemical structures, molecular masses, and monoisotopic masses of saponins from various parts of *P. ginseng*, including roots, flower buds, fruits, and leaves. In addition, we furnish available information about artifactual saponins formed during physicochemical and/or biological treatment and compounds synthesized from saponins isolated from *P. ginseng*.

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Table 1
Scientific and common names of *panax* plants

Scientific name	Rank	Common name
<i>Panax bipinnatifidus</i> Seem	Species	
<i>Panax bipinnatifidus</i> var. <i>angustifolius</i>	Intraspecific taxon	
<i>Panax bipinnatifidus</i> var. <i>bipinnatifidus</i>	Intraspecific taxon	
<i>Panax ginseng</i> C. A. Mey.	Species	Korean ginseng, Ginseng
<i>Panax japonicus</i> (T. Nees) C. A. Mey.	Species	Japanese ginseng
<i>Panax notoginseng</i> (Burkill) F. H. Chen	Species	Chinese ginseng, sanchi
<i>Panax pseudoginseng</i> Wall.	Species	
<i>Panax quinquefolius</i> L.	Species	American ginseng
<i>Panax sokpayensis</i> Shiva K. Sharma & Pandit	Species	
<i>Panax stipuleanatus</i> H. T. Tsai & K. M. Feng	Species	
<i>Panax trifolius</i> L.	Species	
<i>Panax vietnamensis</i> Ha & Grushv.	Species	Vietnamese ginseng
<i>Panax wangianus</i> S. C. Sun	Species	
<i>Panax zingiberensis</i> C. Y. Wu & Feng	Species	

2. Classification of ginseng saponins according to their genin structures

Most ginseng saponins are believed to be biosynthesized from 2,3-oxidosqualene, which is also the precursor of β -sitosterol, a steroid commonly found in plants [13]. It has been suggested that the action of three different enzymes on 2,3-oxidosqualene leads to the formation of cycloartenol, dammarenediol-II, and β -amyrin, the latter two of which are eventually biotransformed into ginseng saponins. Fig. 1 shows the proposed biosynthetic pathway of ginseng saponins and β -sitosterol. Dammarenediol-II is the precursor of dammarane-type saponins, including ginsenosides Rb1, Rb2, Re, and Rg1, which account for a significant portion of saponins found in ginseng species. Dammarane-type saponins are further classified into various groups. By contrast, oleanane-type saponins are biosynthesized from β -amyrin. In *P. ginseng*, however, oleanane-type saponins other than ginsenoside Ro are rare and often practically undetectable.

Table 2 [14–67] displays the molecular formulas, molecular masses, monoisotopic masses, and parts of ginseng saponins, isolated from or related to *P. ginseng*, that are used. We categorize the

ginseng saponins based upon the position of hydroxyl group(s) and/or double bond(s) of their genins.

2.1. Protopanaxadiol, protopanaxatriol, and their glycosides

As shown in Fig. 1, dammarenediol-II is hydroxylated to protopanaxadiol (PPD), 3 β ,12 β ,20-trihydroxydammar-24-ene. Ultimately, a number of saponins are biosynthesized by O-glycosylation of PPD that involves the attachment of saccharide(s) to C-3 and/or C-20. Typical PPD-type saponins include ginsenosides Rb1, Rb2, Rc, and Rd, which are found in the roots [19,20], flower buds [21], and leaves [21] of *P. ginseng*.

PPD may further be hydroxylated to protopanaxatriol (PPT), 3 β ,6 α ,12 β ,20-tetrahydroxydammar-24-ene. A variety of saponins are biosynthesized by O-glycosylation of PPT that involves the attachment of saccharide(s) to C-6 and/or C-20. Typically, the hydroxyl group at C-3 remains free in PPT-type ginsenosides. The two most abundant PPT-type saponins in *P. ginseng* are ginsenosides Re and Rg1.

Fig. 2A illustrates the structures of PPD- and PPT-type saponins. While most naturally occurring ginsenosides are of the (S)-configuration at C-20, some artifactual ginsenosides exist in two epimeric forms at the carbon.

2.2. Peroxidation products of PPD- and PPT-type saponins

Some saponins isolated from the flower buds of *P. ginseng* have an aglycone that is believed to be produced via the peroxidation of PPD or PPT [68]. In most cases, the peroxidation occurs at or around the double bond between C-24 and C-25, and eventually leads to various structures. Fig. 2B, C show the structures of ginsenosides whose genin appears to be produced via the peroxidation of PPD or PPT. Fig. 2B-(a) shows the structures of some saponins that have a hydroperoxyl group at C-24 and a double bond between C-25 and C-26. Fig. 2B-(b) contains the genin structure that has a hydroxyl group at C-24, which would be reduced from the hydroperoxyl group shown in Fig. 2B-(a). In addition, Fig. 2B-(c) shows the structure of floralginsenoside Ta, a glycoside of 3 β ,6 α ,12 β ,20-tetrahydroxydammar-24-one-25-ene, which may be considered to be formed by the dehydration of floralginsenoside Ka, whose structure is illustrated in Fig. 2B-(a).

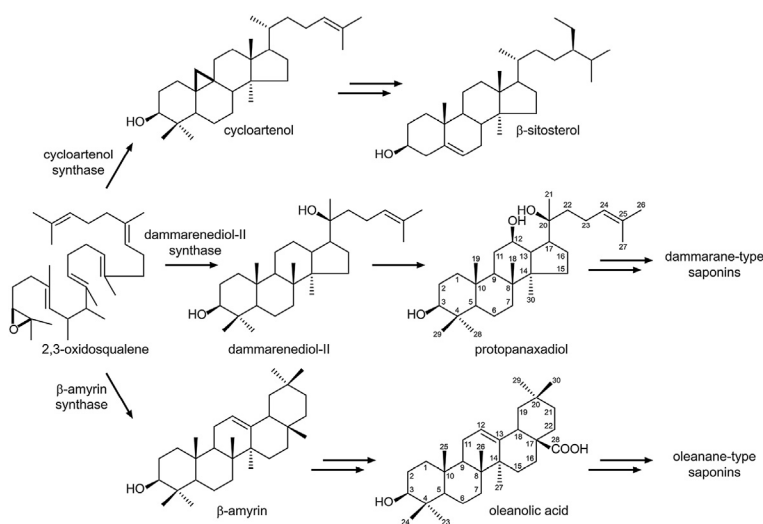


Fig. 1. Biosynthetic pathways of ginseng saponins. 2,3-Oxidosqualene may be cyclized into three different compounds, two of which are dammarenediol-II and β -amyrin, the precursor of dammarane-type saponins and oleanane-type saponins, respectively.

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