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Review

Research progress on chemical diversity of saponins in *Panax ginseng*

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ABSTRACT

Saponins, the major bioactive components of *Panax ginseng* C. A. Mey., are gradually emerging as research hotspots owing to the possession of various pharmacological activities. This review updates the ginsenosides list from *P. ginseng* and the steam-processed ginseng (red ginseng and black ginseng) up to 271 by June of 2024, encompassing 243 saponins from different parts of *P. ginseng* (roots, stems, leaves, flowers, berries, and seeds), 103 from red ginseng, and 65 from black ginseng, respectively. Among 271 saponins, there are a total of 249 (**1**–**249**) dammarane type (with ***a***–***z*** subtypes) tetracyclic triterpene saponins reported from each part of *P. ginseng* and steam-processed ginseng, two (**250**–**251**) lanostane type tetracyclic triterpene saponins identified from red ginseng, 18 (**252**–**269**) oleanane type pentacyclic triterpenoid saponins discovered from each part of *P. ginseng* and steam-processed ginseng, and two (**270**–**271**) ursane type pentacyclic triterpenoid saponins reported from red ginseng. Overall, this review expounds on the chemical diversity of ginsenosides in various aspects, such as chemical structure, spatial distribution and subtype comparison, processed products, and transformation. This facilitates more in-depth research on ginsenosides and contributes to the future development of ginseng.

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1. Introduction

Panax ginseng C. A. Mey. (Renshen in Chinese), known as the king of all herbs, is one of the most important traditional medicine and healthy food in East Asian herbal remedies for over 2 000 years (Piao et al., 2020; Potenza, Montagnani, Santacroce, Charitos & Bottalico, 2023). The traditional medicinal site of ginseng is the root part. In recent years, the research on non-traditional medicinal parts (stems, leaves, flowers, berries, seeds, etc.) has received increasing attention (Tao, Li, Li, & Gong, 2018). Thus far, more than 7 000 articles regarding the chemical constituents of *P. ginseng*

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have been published. In addition, red ginseng and black ginseng, the two main steam-processed products of *P. ginseng*, have the unique chemical profile and the different therapeutic efficacy, are prepared by steaming roots in controlled conditions using fresh or raw ginseng roots and also receive more and more attention (Zhou et al., 2023; Huang, Li, & Wu, 2023; Xu et al., 2023). Red ginseng is obtained through the removal of the branches and roots of fresh ginseng followed by one-time steaming and drying. Black ginseng, on the other hand, is achieved by undergoing steaming and drying multiple times (usually nine times). As a result, the brown–red surface gradually transforms into dark red and ultimately black, which gives it the name black ginseng. Another way of preparing black ginseng is through fermentation (Huang, Li, & Wu, 2023). The main difference of the processing technology between red ginseng and black ginseng lies in the number of steaming times. However, the content of rare ginsenosides in black ginseng is usually higher compared with that in red ginseng (Sun, Pan, & Sung, 2011). As we all know, white ginseng, red ginseng and black ginseng are different in many aspects, including physical properties, processing technologies, phytochemicals, and biological activities. Thus far, more than 2 700 articles regarding the chemical constituents of red ginseng and black ginseng have been published.

It has been confirmed that the pharmacological activities of *P. ginseng* are mainly attributed to the valuable bioactive components ginsenosides. According to the different structures, ginsenosides in *P. ginseng* are commonly divided into two types: damarmane-type tetracyclic triterpenoid saponins (including protopanaxadiol type, protopanaxatriol type, and C17 side-chain varied type), and oleanane type pentacyclic triterpenoid saponins. Studies on ginsenosides have explored various aspects of pharmacology, pharmacodynamics and pharmacochemistry, and great achievements have been acquired. Ginsenosides are known to possess a lot of biological activities including regulatory effects on immunomodulation (You, Cha, & Cho, 2022; Kan et al., 2023), protection functions in the central nervous and cardiovascular systems (Radad, Moldzio, & Rausch, 2011), anti-diabetic (Liu, Deng, & Fan, 2019), anti-aging (Hou, Cui, Kim, Sung, & Choi, 2018), anti-carcinogenic (Li, Li, & Jin, 2023), anti-fatigue (Zhou et al., 2021), anti-stress (Chung et al., 2010) and boosting physical vitality (Hsieh et al., 2023). Actually, ginsenosides are recognized as the key index for quality evaluation of *P. ginseng*. Multi-platform analytical techniques are used in the detection of ginsenosides from *P. ginseng* and its steam-processed products such as thin layer chromatography (TLC), high performance liquid chromatography (HPLC), ultra performance liquid chromatography (UPLC), and liquid chromatography coupled with tandem mass spectrometry (LC-MS). Since the first isolation of six ginsenosides from *P. ginseng* in the 1960s (Elyakov et al., 1964), a total of at least 573 saponin components have been reported from the *Panax* genus by the end of 2020 (Li et al., 2022). In addition, in the phytochemical studies of red ginseng and black ginseng, the number of published reports on ginsenosides is significantly higher than that for other type constituents, including both naturally occurring compounds and those from steaming and biotransformation.

In this review, the reported saponins are classified into tetracyclic triterpenoids and pentacyclic triterpenes. The different types of saponins in various parts of *P. ginseng* (roots, stems, leaves, flowers, berries, and seeds), red ginseng and black ginseng are systematically summarized. Furthermore, the spatial distribution, as well as transformation, are also discussed.

2. Damarane type tetracyclic triterpenoid saponins

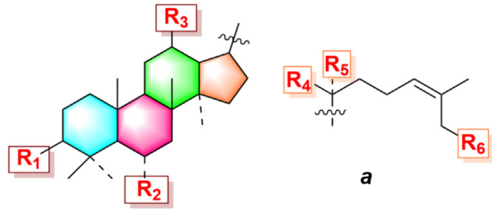
Dammarane type tetracyclic triterpene saponins are generated from the full chair conformation of epoxy squalene. The structure of this type saponin exhibits certain distinguishable features, such as angular methyl at C-8 in β configuration, a β-H at C-13, a β-CH_3 at C-10, a side chain at C-17 in β configuration, and the C-20 configuration being either *R* or *S* (the majority being *S*). In addition, glucose (glu), glucuronic acid (gluA), rhamnose (rha), xylose (xyl), and arabinose (ara) are five most common monosaccharides in the structure of ginsenosides, with arabinose appearing either in the pyran (arap) or furan (araf) configuration.

According to the different classification methods, dammarane type tetracyclic triterpene ginsenosides are classified into different types. For example, according to the natural abundance, ginsenosides could be divided into macro ginsenosides (such as ginsenosides Rb_1, Re, Rd, etc.) and rare ginsenosides (normally < 0.1%, such as Rg_5, Rk_1, Rg_3, etc). According to the hydroxyl group connected to C-6, ginsenosides are generally classified into protopanaxadiol (PPD, the hydroxyl group is not connected to C-6) type and protopanaxatriol (PPT, the hydroxyl group is connected to C-6) type. With more and more ginsenosides being isolated and identified, the structure of ginsenosides has also undergone more and more changes, especially the changes in the side chain. The above classification methods cannot meet the structural diversity of ginsenosides. So, in this review, according to the alterations of the side chain and the tetracyclic skeleton, the dammarane type tetracyclic triterpene saponins (**1**–**249**) reported from each part of *P. ginseng* and steam-processed ginseng were classified into subtypes from ***a*** to ***z*** (Figs. 1–3). And the name, subtype, formula, accurate molecular mass and sources were summarized in Table 1.

Among these subtypes, the C-17 side chain in subtypes ***a*** to ***h*** contains one carbon–carbon double bonds, the C-17 side chain in subtypes ***i*** to ***o*** contains two carbon–carbon double bond, while the C-17 side chain in subtypes ***p*** and ***q*** contains no double bond. Moreover, a cleavage chain occurs in ***r*** and ***s***, a ring formed by the side chain in subtypes ***t*** to ***v***, a hydroxylation at C-7 in subtype ***w***, an oxidation at C-3 in subtype ***x***, and an oxidation at C-12 in subtype ***y***, a dehydration at C-6 in subtype ***z***. In terms of the ^{13}C NMR spectroscopic properties, the ***a*** subtype saponins are characterized by two downfield signals at δ_C 126 and 131 assigned to C-24 and C-25, respectively, the ***b*** to ***e*** subtypes saponins are characterized by δ_C 140 signal assigned to C-20; the ***f*** subtype saponins are characterized by δ_C 138 and 127 signals assigned to C-22 and C-23; the ***g*** subtype saponins are characterized by δ_C 126 and 138 signals assigned to C-23 and C-24 (Li, Liu, & Lu, 2012). It should also be highlighted that the *E*/*Z* geometric isomerism exists when the resultant double bond is formed between C-20 and C-22, and the majority of them are the *E*-form isomers rather than the *Z*-form. In addition, subtype ***k*** is of the *Z*-form, with the δ_C of C-21 being 27.5, and subtype ***l*** is *E*-form with the δ_C of C-21 being 13.1 (Li, Liu, & Lu, 2012).

A total of 192 ginsenosides (**1**–**192**) belonging to subtypes ***a*** to ***h*** were identified from ginseng and steam-processed ginseng. Among subtypes ***a*** to ***h***, subtype ***a*** (C=C at C-24, 25) composed of PPD-type and PPT-type account for the largest proportion (143 saponins, 74.5%). While subtypes ***b*** to ***h*** with the heterotopic double bond at C20(22), C22(23), C23(24) or C25(26) accounts for the remaining proportion (49 saponins, 25.5%). It is worth mentioning that the five saponins (**153**–**157**) belonging to ***f*** subtype with the double bond existing at C22(23) were only reported from the root part. Moreover, for these saponins containing one double bond in C-17 side chain, if calculated based on their discovery sources respectively, 110, 74, 101, 46, 62 and 48 ginsenosides have been reported in root, stem & leaf, flower, berry & seed, red ginseng (RG) and black ginseng (BG), respectively.

A total of 33 ginsenosides (**193**–**225**) belonging to subtypes ***i*** to ***o*** were identified from ginseng and steam-processed ginseng. The double bonds at C-20(22), 24(25) (subtype ***k*** and ***l***) take up the largest proportion (17 saponins, 51.5%), while the double bonds at C-



1 R_1=OH, R_2=H, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
2 R_1=OH, R_2=H, R_3=OH, R_4=CH_3, R_5=OH, R_6=H, 20R
3 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap$^{4\text{-}1}$xyl, R_5=CH_3, R_6=H
4 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf$^{2\text{-}1}$xyl, R_5=CH_3, R_6=H
5 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu$^{3\text{-}1}$xyl, R_5=CH_3, R_6=H
6 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-butenoyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap$^{4\text{-}1}$xyl, R_5=CH_3, R_6=H
7 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-acteyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap$^{4\text{-}1}$xyl, R_5=CH_3, R_6=H
8 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-butenoyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
9 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-butenoyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
10 R_1=*O*-glu$^{2\text{-}1}$glu^{4}-butenoyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
11 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-butenoyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
12 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
13 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
14 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$xyl, R_5=CH_3, R_6=H
15 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
16 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
17 R_1=*O*-glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
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19 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
20 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=CH_3, R_5=OH, R_6=H, 20R
21 R_1=*O*-glu, R_2=H, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
22 R_1=*O*-glu, R_2=H, R_3=OH, R_4=CH_3, R_5=OH, R_6=H, 20R
23 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-acteyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
24 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-acteyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
25 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-acteyl, R_2=H, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
26 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-acteyl, R_2=H, R_3=OH, R_4=CH_3, R_5=OH, R_6=H, 20R
27 R_1=*O*-glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
28 R_1=OH, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
29 R_1=OH, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
30 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-butenoyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$rha, R_5=CH_3, R_6=H
31 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$rha, R_5=CH_3, R_6=H
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34 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-acteyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
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36 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-acteyl, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
37 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-mal, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu$^{3\text{-}1}$xyl, R_5=CH_3, R_6=H
38 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-mal, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
39 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-mal, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
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45 R_1=*O*-glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
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48 R_1=*O*-glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
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56 R_1=*O*-glu$^{2\text{-}1}$glu^{3}-mal, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
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58 R_1=OH, R_2=OH, R_3=OH, R_4=CH_3, R_5=OH, R_6=H, 20R
59 R_1=OH, R_2=OH, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
60 R_1=OH, R_2=OH, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
61 R_1=OH, R_2=OH, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
62 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
63 R_1=OH, R_2=*O*-glu$^{3\text{-}1}$glu, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
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67 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$glu, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
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73 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$rha, R_3=OH, R_4=OH, R_5=CH_3, R_6=H, 20R
74 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
75 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=CH_3, R_5=OH, R_6=H, 20R
76 R_1=*O*-glu, R_2=OH, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
77 R_1=OH, R_2=*O*-glu^{6}-acetyl, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
78 R_1=OH, R_2=*O*-(6-acetyl)glu$^{2\text{-}1}$rha, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
79 R_1=OH, R_2=*O*-glu^{6}-mal, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
80 R_1=OH, R_2=*O*-(6-mal)glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
81 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$xyl, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
82 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$xyl, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
83 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$xyl, R_3=OH, R_4=OH, R_5=CH_3, R_6=H, 20R
84 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
85 R_1=OH, R_2=*O*-glu^{6}-acteyl, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
86 R_1=OH, R_2=*O*-glu^{6}-butenoyl, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
87 R_1=OH, R_2=*O*-xyl, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
88 R_1=OH, R_2=OH, R_3=H, R_4=*O*-glu$^{6\text{-}1}$xyl, R_5=CH_3, R_6=H
89 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=OCH_3, R_5=CH_3, R_6=H
90 R_1=*O*-glu, R_2=OH, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
91 R_1=COOH, R_2=OH, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
92 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
93 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
94 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=OH, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
95 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu^{2}-mal, R_5=CH_3, R_6=H
96 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu^{4}-mal, R_5=CH_3, R_6=H
97 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=OH, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
98 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=OCH_3, R_5=CH_3, R_6=H, 20R
99 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=OCH_3, R_5=CH_3, R_6=H
100 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=OCH_3, R_5=CH_3, R_6=H, 20R
101 R_1=*O*-glu$^{2\text{-}1}$glu$^{2\text{-}1}$xyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$xyl$^{4\text{-}1}$xyl, R_5=CH_3, R_6=H
102 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=H, R_4=*O*-glu, R_5=CH_3, R_6=H
103 R_1=OH, R_2=*O*-malonyl methyl, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
104 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-butenoyl, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
105 R_1=*O*H, R_2=*O*-(6-mal)glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
106 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-(4-mal)glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
107 R_1=*O*-glu$^{2\text{-}1}$glu^{3}-mal, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
108 R_1=*O*-glu$^{2\text{-}1}$glu^{2}-mal, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
109 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-mal, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$xyl, R_5=CH_3, R_6=H
110 R_1=OH, R_2=*O*-(6-acetyl)glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
111 R_1=OH, R_2=*O*-acetyl, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
112 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H, 20R
113 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-acteyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
114 R_1=*O*-acetyl, R_2=OH, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
115 R_1=OH, R_2=*O*-arap$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
116 R_1=*O*-glu$^{2\text{-}1}$xyl, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
117 R_1=*O*-(6-butenoyl)glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
118 R_1=OH, R_2=*O*-glu$^{4\text{-}1}$glu, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
119 R_1=OH, R_2=*O*-(6-acetyl)glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
120 R_1=*O*-glu$^{2\text{-}1}$arap, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
121 R_1=*O*-glu$^{2\text{-}1}$glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-arap, R_5=CH_3, R_6=H
122 R_1=*O*-glu$^{2\text{-}1}$glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu, R_5=CH_3, R_6=H
123 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$xyl, R_5=CH_3, R_6=H
124 R_1=*O*-glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$glu$^{6\text{-}1}$xyl, R_5=CH_3, R_6=H
125 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
126 R_1=*O*-(6-acetyl)glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$xyl, R_5=CH_3, R_6=H
127 R_1=*O*-(6-acetyl)glu$^{2\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
128 R_1=OH, R_2=*O*-glu^{6}-acetyl, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
129 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-mal, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$xyl$^{4\text{-}1}$arap, R_5=CH_3, R_6=H
130 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-mal, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf$^{2\text{-}1}$xyl, R_5=CH_3, R_6=H
131 R_1=*O*-glu, R_2=OH, R_3=OH, R_4=OH, R_5=CH_3, R_6=H
132 R_1=*O*-glu$^{6\text{-}1}$glu, R_2=H, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=H
133 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$glu, R_3=OH, R_4=OH, R_5=CH_3, R_6=OH
134 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$glu, R_3=OH, R_4=OH, R_5=CH_3, R_6=OH
135 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=*O*-glu$^{2\text{-}1}$rha, R_5=CH_3, R_6=H
136 R_1=OH, R_2=*O*-glu$^{4\text{-}1}$glu, R_3=OH, R_4=*O*-glu^{6}-acteyl, R_5=CH_3, R_6=H
137 R_1=*O*-glu$^{2\text{-}1}$glu^{6}-actey, R_2=H, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$araf, R_5=CH_3, R_6=H
138 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-mal, R_5=CH_3, R_6=H
139 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$rha, R_3=OH, R_4=*O*-glu$^{2\text{-}1}$glu, R_5=CH_3, R_6=H
140 R_1=OH, R_2=*O*-glu, R_3=OH, R_4=*O*-glu$^{6\text{-}1}$arap, R_5=CH_3, R_6=H
141 R_1=OH, R_2=*O*-glu$^{2\text{-}1}$glu, R_3=OH, R_4=OH, R_5=CH_3, R_6=OH
142 R_1=OH, R_2=OH, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=OH
143 R_1=OH, R_2=OH, R_3=OH, R_4=*O*-glu, R_5=CH_3, R_6=OH

Fig. 1. Subtype ***a*** of damarane type tetracyclic triterpenoid saponins.

20(21), 24(25) (subtype ***i*** and ***j***) take up the second largest proportion (12 saponins, 36.4%), and the subtype ***i*** (11 saponins) appears to be more prevalent than subtype ***j*** (one saponin). Among ***i*** to ***o*** subtypes saponins, based on their discovery sources, there are

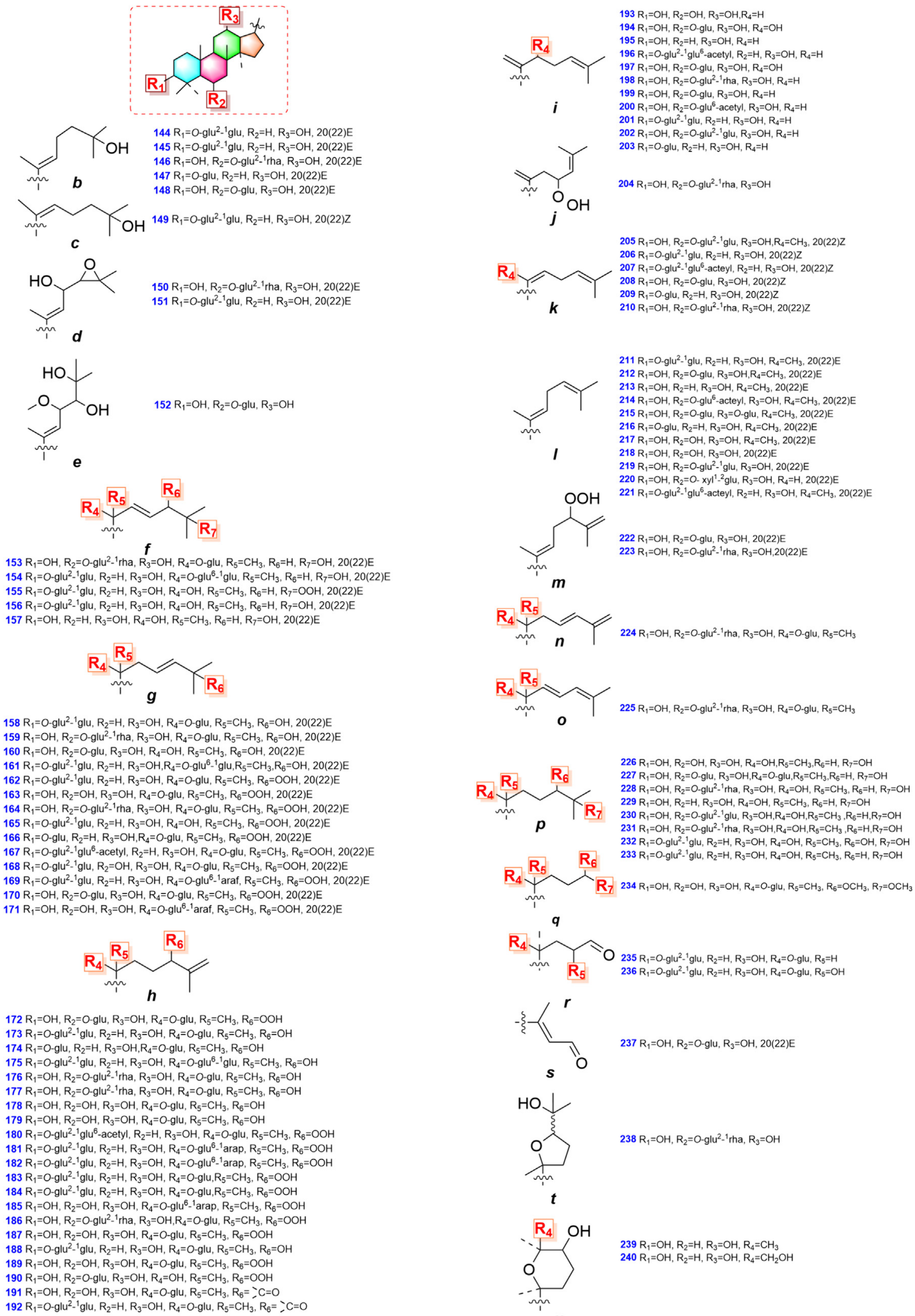

Fig. 2. Subtype ***b*–*u*** of damarane type tetracyclic triterpenoid saponins.

22, seven, eight, seven, 20 and 13 saponins identified from root, stem & leaf, flower, berry & seed, RG and BG, respectively. Furthermore, two saponin (**222**, **223**) with double bonds at C-20(22), 25(26) (subtype ***m***) was reported from the leaf part, one saponin

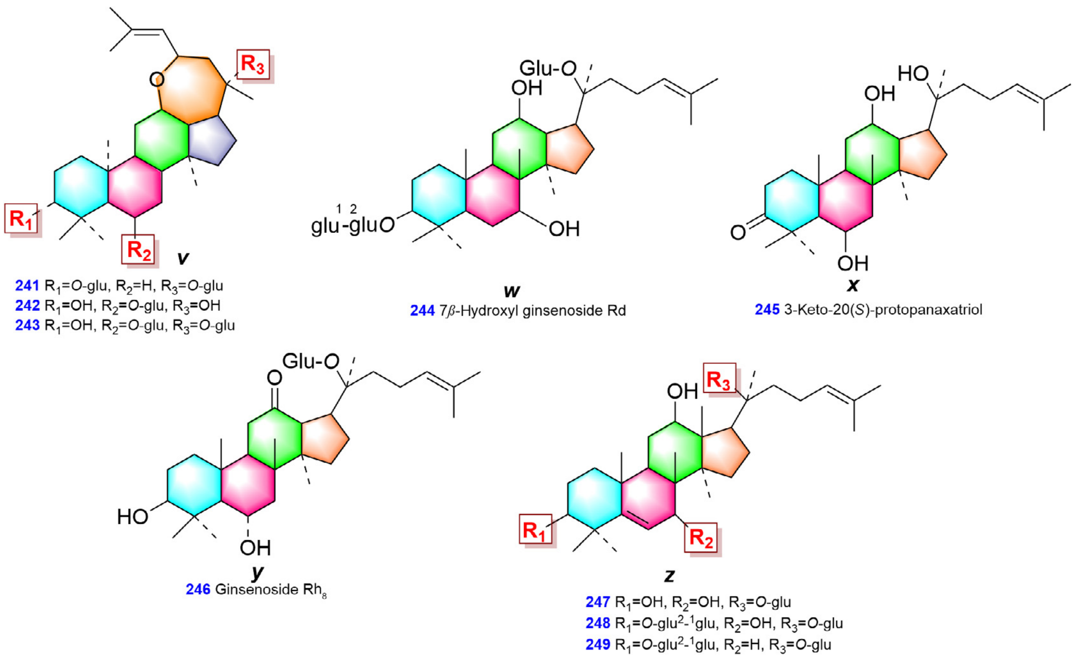

Fig. 3. Subtype ***v*–*z*** of damarane type tetracyclic triterpenoid saponins.

(**224**) with double bonds at C-23(24), 25(26) (subtype ***n***) and one saponin (**225**) with double bonds at C-22(23), 24(25) (subtype ***o***) were reported from the root part. Overall, saponins with two double bonds mainly existed in root part of ginseng, red ginseng and black ginseng.

A total of nine ginsenosides (**226**–**234**) belonging to subtypes ***p*** to ***q*** were identified from ginseng and steam-processed ginseng. Among ***p*** to ***q*** subtypes saponins, calculated based on their discovery sources, there are two, one, three, three and three saponins reported from root, stem & leaf, flower, berry & seed, and RG, respectively.

A total of three ginsenosides (**235**–**237**) belonging to subtypes ***r*** to ***s*** with a cleavage side chain were identified from ginseng and steam-processed ginseng. Among ***r*** to ***s*** subtypes saponins, calculated based on their discovery sources, there are two and one saponins reported from flower and BG, respectively.

A total of six ginsenosides (**238**–**243**) belonging to subtypes ***t*** to ***v*** with a ring side chain were identified from ginseng and steam-processed ginseng. Among these subtypes, the saponin (**238**) possessing a 20, 24-epoxy furan ring (subtypes ***t***) at the C17 side chain is reported from the root, stem, leaf, RG and BG; the two saponins (**239, 240**) with a 20, 25-epoxy pyran ring (subtypes ***u***) merely reported from RG; while the three saponins (**241**–**243**) with a 12, 24-epoxy seven-membered oxygen-containing ring (subtypes ***v***) are identified from the leaf and flower part of ginseng.

Besides the changes in the side chain, there are also six saponins discovered with the changes in the tetracyclic skeleton, such as hydroxylation at C-7 in subtype ***w*** (**244**), oxidation at C-3 in subtype ***x*** (**245**), oxidation at C-12 in subtype ***y*** (**36**), 5,6-dehydroxylation in subtype ***z*** (**247**–**249**). And these saponins with changing tetracyclic skeleton are reported from flower, root, leaf, seed, RG and BG.

3. Lanostane type tetracyclic triterpenoid saponins

Lanostane type tetracyclic triterpene saponins are formed by cyclization of epoxy squalene in a chair-boat–chair conformation. The β-CH_3, β-CH_3, and α-CH_3 are connected to C-10, C-13, and C-14, respectively. The position C-20 has an *R* configuration. And the A/B, B/C, and C/D rings are all *trans*. In terms of the ^{13}C NMR spectroscopic characteristics, there exist four olefinic carbon signals and seven methyl groups. The δ_C values of C-5, C-6, C-24 and C-25 are typically 140.5, 124.3, 125.8 and 132.2 (CD_3OD), respectively (Chung et al., 2014).

A total of two saponins (**250**–**251**) belonging to lanostane type tetracyclic triterpene were identified from red ginseng (Table 2, Fig. 4).

4. Oleanane type pentacyclic triterpenoid saponins

The biosynthesis of triterpenoid saponins starts from 2,3-oxidosqualene, which is synthesized through the mevalonic acid pathway. Dammarene diol-II synthase is responsible for the formation of the dammarane skeleton, while β-amyrin synthase can catalyze the cyclization of oxidosqualene to generate the oleanane skeleton, and then followed by β-amyrin 28-oxidase to modify β-amyrin into oleanolic acid (Tang et al., 2019; Tansakul, Shibuya, Kushiro & Ebizuka, 2006; Kushiro, Shibuya & Ebizuka, 1998; Han, Kim, Ban, Hwang, & Choi, 2013).

The ^{13}C NMR spectra show significant differences from those of the tetracyclic triterpenoid saponins. There are seven methyls, δ_C of C-28 is about 180, two olefinic carbons at δ_C 122 and 145 are attributed to C-12 and C-13, and another carbonyl carbon is typical for the primary glucuronic acid residue in most cases, which can be used to rapidly characterize this type saponin.

In ginseng or steam-processed ginseng, the sapogenins of the identified oleanane type pentacyclic triterpenoid saponins are all oleanolic acid (Table 3, Fig. 5). A total of 18 (**252**–**269**) oleanane type pentacyclic triterpenoid saponins were discovered. Among them, there are ten, five, two, two, ten and one saponins respectively found in the root, stem & leaf, flower, berry & seed, red ginseng and black ginseng.

5. Ursane type pentacyclic triterpenoid saponins

Ursane type triterpenoids, also known as α-amylane type, are mostly a derivative of ursolic acid. The A/B, B/C, and C/D rings are all *trans*, while the D/E ring is mostly *cis* condensed, and there

Table 1
Information of 249 saponins of damarane type tetracyclic triterpenoid saponins.

No.	Compounds	Subtype	Formula	Accurate molecular mass	References
1	Protopanaxadiol	***a***	$C_{30}H_{52}O_3$	460.391 6	Root and Stem (Zhu, 2020), Leaf (Gong et al., 2023), Berry (Wang et al., 2007), RG and BG (Li et al., 2023)
2	20(*R*)-protopanaxadiol	***a***	$C_{30}H_{52}O_3$	460.391 6	Leaf (Zhang et al., 1989), Berry (Piao et al., 2020)
3	Ginsenoside Ra_1	***a***	$C_{58}H_{98}O_{26}$	1 210.634 6	Root (Lee et al., 2017a), RG (Lee et al., 2018), BG (Wang et al., 2023c)
4	Ginsenoside Ra_2	***a***	$C_{58}H_{98}O_{26}$	1 210.634 6	Root (Lee et al., 2017a), RG (Zhou, Xu, & Yang, 2016), BG (Wang et al., 2023c)
5	Ginsenoside Ra_3	***a***	$C_{59}H_{100}O_{27}$	1 240.645 2	Root (Lee et al., 2017a), RG (Zhou, Xu, & Yang, 2016), BG (Wang et al., 2023c)
6	Ginsenoside Ra_4	***a***	$C_{62}H_{102}O_{27}$	1 278.660 8	Root (Zhu et al., 2011)
7	Ginsenoside Ra_5	***a***	$C_{60}H_{100}O_{27}$	1 252.645 2	Root (Zhu et al., 2011)
8	Ginsenoside Ra_6	***a***	$C_{58}H_{96}O_{24}$	1 176.629 2	Root (Zhu et al., 2011), RG and BG (Wang et al., 2023c)
9	Ginsenoside Ra_7	***a***	$C_{57}H_{94}O_{23}$	1 146.618 6	Root (Zhu et al., 2011)
10	Ginsenoside Ra_8	***a***	$C_{57}H_{94}O_{23}$	1 146.618 6	Root (Zhu et al., 2011), Berry (Kim, Kaygusuz, Lee, & Jeong, 2021)
11	Ginsenoside Ra_9	***a***	$C_{57}H_{94}O_{23}$	1 146.618 6	Root (Zhu et al., 2011)
12	Ginsenoside Rb_1	***a***	$C_{54}H_{92}O_{23}$	1 108.602 9	Root and Berry (Lee et al., 2017a), Stem (Zhu, 2020), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Rho et al., 2020), RG (Zhou et al., 2023), BG (Li et al., 2023)
13	Ginsenoside Rb_2	***a***	$C_{53}H_{90}O_{22}$	1 078.592 4	Root and Berry (Lee et al., 2017a), Stem (Zhu, 2020), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Rho et al., 2020), RG (Zhou et al., 2023), BG (Wang et al., 2023c)
14	Ginsenoside Rb_3	***a***	$C_{53}H_{90}O_{22}$	1 078.592 4	Root and Berry (Lee et al., 2017a), Stem (Zhu, 2020), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), RG (Zhou et al.,2023), BG (Qi et al., 2023)
15	Ginsenoside Rc	***a***	$C_{53}H_{90}O_{22}$	1 078.592 4	Root (Lee et al., 2017a), Stem and Leaf(Zhu, 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Berry (Tao, Li, Li, & Gong, 2018), Seed (Leng, 2007), RG (Zhou et al., 2023), BG (Qi et al., 2023)
16	Ginsenoside Rd	***a***	$C_{48}H_{82}O_{18}$	946.550 1	Root and Berry (Lee et al., 2017a), Stem (Zhu, 2020), Leaf (Yang et al., 2019), Flower (Wu, Lu, Teng, Guo, &Liu, 2016), Seed (Rho et al., 2020), RG (Zhou et al., 2023), BG (Li et al., 2023)
17	Ginsenoside Rd_2	***a***	$C_{47}H_{80}O_{17}$	916.539 6	Root (Sang, Dong, & Hong, 2008), Leaf (Piao et al., 2020), RG and BG (Wang et al., 2023c)
18	Ginsenoside F_2	***a***	$C_{42}H_{72}O_{13}$	784.497 3	Root and Berry and Leaf (Lee et al., 2017a), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), RG and BG (Li et al., 2023)
19	Ginsenoside Rg_3	***a***	$C_{42}H_{72}O_{13}$	784.497 3	Root and Berry (Lee et al., 2017a), Stem (Zhu, 2020), Leaf (Piao et al., 2017), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Leng, 2007), RG (Sun, Gao, Zhao, & Cheng, 2013), BG (Wang et al., 2023c)
20	20(*R*)-ginsenoside Rg_3	***a***	$C_{42}H_{72}O_{13}$	784.497 3	Root (Yang, Hu,Wu, Ye, & Guo, 2014), Leaf (Piao et al., 2020), Flower (Shi et al., 2020), Berry (Xu, Zhan, & Zhang, 2007), RG(Zhou et al., 2023), BG (Wang et al., 2023c)
21	Ginsenoside Rh_2	***a***	$C_{36}H_{62}O_8$	622.444 5	Root and Stem (Zhu, 2020), Leaf (Piao et al., 2020), Berry (Wang et al., 2007), Seed (Leng, 2007), RG and BG (Wang et al., 2023c)
22	20(*R*)-ginsenoside Rh_2	***a***	$C_{36}H_{62}O_8$	622.444 5	Root (Zhu, 2020), Leaf (Piao et al., 2020), Berry (Zhao, Yuan, & Lv, 1991), RG and BG (Wang et al., 2023c)
23	Ginsenoside Rs_1	***a***	$C_{55}H_{92}O_{23}$	1 120.602 9	Root (Yang et al., 2016), Flower (Shi et al., 2020), RG (Zhou, Xu, & Yang, 2016), BG (Wang et al., 2023c)
24	Ginsenoside Rs_2	***a***	$C_{55}H_{92}O_{23}$	1 120.602 9	Root (Zhu et al., 2011), Stem and Leaf (Gong et al., 2023), RG and BG (Wang et al., 2023c)
25	Ginsenoside Rs_3	***a***	$C_{44}H_{74}O_{14}$	826.507 9	Root (Zhu, 2020), Flower (Shi et al., 2020), RG (Zhou, Xu, & Yang, 2016), BG (Sun, Pan, & Sung, 2011)
26	20(*R*)-ginsenoside Rs_3	***a***	$C_{44}H_{74}O_{14}$	826.507 9	Root (Chen, Balan, & Propovich, 2020), RG (Zhou, Xu, & Yang, 2016), BG (Sun, Pan, & Sung, 2011)
27	Ginsenoside compound O	***a***	$C_{47}H_{80}O_{17}$	916.539 6	Root and Berry (Lee et al., 2017a), Leaf (Piao et al., 2020), BG (Lee et al., 2018)
28	Ginsenoside compound Y	***a***	$C_{41}H_{70}O_{12}$	754.486 7	Root (Lee et al., 2017a), Leaf (Piao et al., 2020), Stem (Quan, Jin, Min, Kim, & Yang, 2012), RG (Zhou et al., 2023), BG (Lee et al., 2018)
29	Ginsenoside compound K	***a***	$C_{36}H_{62}O_8$	622.444 5	Root and Berry (Lee et al., 2017a), Leaf (Piao et al., 2020), Flower (Zhang et al., 2007), RG and BG (Li et al., 2023)
30	Ginsenoside IV	***a***	$C_{58}H_{96}O_{24}$	1 176.629 2	Root (Yang et al., 2012)
31	Gypenoside V	***a***	$C_{54}H_{92}O_{22}$	1 092.608 0	Root (Yang et al., 2012)
32	Ginsenoside Mc	***a***	$C_{41}H_{70}O_{12}$	754.486 7	Leaf (Piao et al., 2020), Flower (Li & Gong, 2019), RG (Zhou et al., 2023)
33	Acetyl-ginsenoside Rb_1	***a***	$C_{56}H_{96}O_{24}$	1 152.629 2	Root (Chen, Balan, & Propovich, 2020), Leaf (Piao et al., 2020), RG (Xu et al., 2016b)
34	Acetyl-ginsenoside Rc	***a***	$C_{55}H_{92}O_{23}$	1 120.602 9	Root (Chen, Balan, & Propovich, 2020) and Leaf (Piao et al., 2020)
35	Acetyl-ginsenoside Rb_3	***a***	$C_{55}H_{92}O_{23}$	1 120.602 9	Root (Chen, Balan, & Propovich, 2020) and Leaf (Piao et al., 2020)
36	Acetyl-ginsenoside Rd	***a***	$C_{50}H_{84}O_{19}$	988.560 7	Root (Chen, Balan, & Propovich, 2020)
37	Malonyl-ginsenoside Ra_3	***a***	$C_{62}H_{102}O_{30}$	1 326.645 6	Root (Ruan et al., 2010)
38	Malonyl-ginsenoside Rb_1	***a***	$C_{57}H_{94}O_{26}$	1 194.603 3	Root and Berry (Lee et al., 2017a), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Zheng, Lei, Wang, Feng, & Wang, 2019), RG (Lee et al., 2018)
39	Malonyl-ginsenoside Rb_2	***a***	$C_{56}H_{92}O_{25}$	1 164.592 8	Root and Berry (Lee et al., 2017a), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), RG (Lee et al., 2018)
40	Malonyl-ginsenoside Rb_3	***a***	$C_{56}H_{92}O_{25}$	1 164.592 8	Root (Chen, Balan, & Propovich, 2020), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016)

Table 1 (*continued*)

No.	Compounds	Subtype	Formula	Accurate molecular mass	References
41	Malonyl-ginsenoside Rc	***a***	$C_{56}H_{92}O_{25}$	1 164.592 8	Root and Leaf and Berry (Lee et al., 2017a), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), RG(Lee et al., 2018)
42	Malonyl-ginsenoside Rd	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Root and Berry (Lee et al., 2017a), Leaf (Piao et al.,2020) Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Zheng, Lei, Wang, Feng, & Wang, 2019), RG (Xu et al., 2016b)
43	Notoginsenoside Fe	***a***	$C_{47}H_{80}O_{17}$	916.539 6	Root (Chen, Balan, & Popovich, 2020), Flower (Shi et al., 2020), Berry (Tao, Li, Li, & Gong, 2018), Leaf (Piao et al., 2020), RG and BG (Wang et al., 2023c)
44	Malonyl-notoginsenoside R_4	***a***	$C_{62}H_{102}O_{30}$	1 326.645 6	Root (Sun et al 2007)
45	Gypenoside XVII	***a***	$C_{48}H_{82}O_{18}$	946.550 1	Root (Zhu et al., 2011), Leaf (Piao et al., 2020), Flower (Shi et al., 2020), Berry (Tao, Li, Li, & Gong., 2018), RG and BG (Wang et al., 2023c)
46	Gypenoside IX	***a***	$C_{47}H_{80}O_{17}$	916.539 6	Leaf (Yang et al., 2019), Berry (Lee, Seo, Singh, Lee, & Lee, 2020)
47	Pseudoginsenoside Rc_1	***a***	$C_{50}H_{84}O_{19}$	988.560 7	Root (Zhu et al., 2011), Flower (Li & Gong, 2019), Berry (Tao, Li, Li, & Gong, 2018), RG (Xu et al., 2016b)
48	Quinquenoside L_{10}	***a***	$C_{47}H_{80}O_{17}$	916.539 6	Root (Zhu, 2020), Stem and Leaf (Xue, Wang, Yu, Guo, & Wang, 2021), Flower (Li & Gong, 2019), Berry (Tao, Li, Li, & Gong, 2018)
49	Malonyl-floralginsenoside Rd_2	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Flower (Qiu et al., 2017)
50	Malonyl-floralginsenoside Rd_3	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Flower (Qiu et al., 2017)
51	Malonyl-floralginsenoside Rd_4	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Flower (Qiu et al., 2017)
52	Malonyl-floralginsenoside Rd_5	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Flower (Qiu et al., 2017)
53	Malonyl-floralginsenoside Rd_6	***a***	$C_{54}H_{86}O_{24}$	1 118.550 9	Flower (Qiu et al., 2017)
54	Malonyl-floralginsenoside Rc_2	***a***	$C_{56}H_{92}O_{25}$	1 164.592 8	Flower (Qiu et al., 2017)
55	Malonyl-floralginsenoside Rc_3	***a***	$C_{56}H_{92}O_{25}$	1 164.592 8	Flower (Qiu et al., 2017)
56	Malonyl-floralginsenoside Rc_4	***a***	$C_{56}H_{92}O_{25}$	1 164.592 8	Flower (Qiu et al., 2017)
57	Protopanaxatriol	***a***	$C_{30}H_{52}O_4$	476.386 6	Root and Stem (Zhu, 2020), Leaf (Li et al., 2023), Berry (Xu, Zhan, & Zhang, 2007), Seed (Zhu, 2020), RG and BG (Li et al., 2023)
58	20(*R*)-protopanaxatriol	***a***	$C_{30}H_{52}O_4$	476.386 6	Root (Zhu et al., 2018), Leaf (Dou, Wen, Weng, Pei & Chen, 1997), Berry (Xu, Zhan, & Zhang, 2007)
59	Ginsenoside F_1	***a***	$C_{36}H_{62}O_9$	638.439 4	Root (Zhu et al., 2018), Leaf (Shin, Kwon, & Park,2015), Flower (Nguyen et al., 2010), Berry (Lee et al., 2017a), RG (Wang et al., 2023c), BG (Qi et al., 2023)
60	Ginsenoside F_3	***a***	$C_{41}H_{70}O_{13}$	770.481 6	Root (Zhu et al., 2018), Leaf (Shin, Kwon, & Park, 2015), Flower (Li, Xu, & Gong, 2016), Berry (Lee et al., 2017a), RG (Zhou et al., 2023), BG (Qi et al., 2023)
61	Ginsenoside F_5	***a***	$C_{41}H_{70}O_{13}$	770.481 6	Root (Zhu et al., 2018), Leaf (Shin, Kwon, & Park, 2015), Flower (Nguyen et al., 2010), Berry (Lee et al., 2017a), RG (Zhou et al., 2023), BG (Qi et al., 2023)
62	Ginsenoside Re	***a***	$C_{48}H_{82}O_{18}$	946.550 1	Root and Berry (Lee et al., 2017a), Stem (Zhu, 2020), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Rho et al., 2020), RG (Zhou et al., 2023), BG (Qi et al., 2023)
63	Ginsenoside Re_2	***a***	$C_{48}H_{82}O_{19}$	962.545 0	Root (Wang et al., 2023b), Flower (Shi et al., 2020), RG (Zhou, Xu, & Yang, 2016), BG (Qi et al., 2023)
64	Ginsenoside Re_3	***a***	$C_{48}H_{82}O_{19}$	962.545 0	Root (Wang et al., 2023b), Flower (Shi et al., 2020)
65	Ginsenoside Re_4	***a***	$C_{47}H_{80}O_{18}$	932.534 5	Root (Wang et al., 2023b), Stem and Leaf(Shin, Kwon, & Park, 2015)
66	Ginsenoside Re_6	***a***	$C_{46}H_{76}O_{15}$	868.518 4	Root (Zhu et al., 2011)
67	Ginsenoside Rf	***a***	$C_{42}H_{72}O_{14}$	800.492 2	Root (Lee et al., 2017a), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Berry (Kim, Kaygusuz, Lee, & Jeong, 2021), RG (Zhou, Xu, & Yang, 2016), BG (Qi et al., 2023)
68	20(*R*)-ginsenoside Rf	***a***	$C_{42}H_{72}O_{14}$	800.492 2	RG (Zhou, Xu, & Yang, 2016)
69	20-*O*-glucoginsenoside Rf	***a***	$C_{48}H_{82}O_{19}$	962.545 0	Root and Flower (Lee et al., 2017a), Leaf (Piao et al., 2020), RG (Zhou, Xu, & Yang, 2016), BG(Wang et al., 2023c)
70	20(*S*)-ginsenoside Rf-1a	***a***	$C_{42}H_{72}O_{14}$	800.492 2	Root (Chen, Balan, & Propovich, 2020), RG (Zhou, Xu, & Yang, 2016)
71	Ginsenoside Rg_1	***a***	$C_{42}H_{72}O_{14}$	800.492 2	Root and Berry (Lee et al., 2017a), Stem and Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Rho et al., 2020), RG (Zhou et al., 2023), BG (Qi et al., 2023)
72	Ginsenoside Rg_2	***a***	$C_{42}H_{72}O_{13}$	784.497 3	Root and Berry (Lee et al., 2017a), Stem (Zhu, 2020), Leaf (Gong et al., 2023), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Rho et al., 2020), RG (Zhou, Xu, & Yang, 2016), BG (Qi et al., 2023)

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Table 1 (*continued*)

No.	Compounds	Subtype	Formula	Accurate molecular mass	References
73	20(*R*)-ginsenoside Rg_2	***a***	$C_{42}H_{72}O_{13}$	784.497 3	Root (Lee et al., 2017a), Leaf (Piao et al., 2020) , Flower (Li & Gong, 2019), Berry (Lee et al., 2017a), RG (Zhou, Xu, & Yang, 2016), BG (Qi et al., 2023)
74	Ginsenoside Rh_1	***a***	$C_{36}H_{62}O_9$	638.439 4	Root (Wang et al., 2023b), Stem and Leaf (Gong et al., 2023), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Berry (Lee et al., 2017a), RG (Zhou, Xu, & Yang, 2016), BG (Qi et al., 2023)
75	20(*R*)-ginsenoside Rh_1	***a***	$C_{36}H_{62}O_9$	638.439 4	Root (Yang et al., 2023), Leaf (Piao et al., 2020), Flower (Shi et al., 2020), RG and BG (Wang et al., 2023c)
76	Ginsenoside Ia	***a***	$C_{42}H_{72}O_{14}$	800.492 2	Leaf (Dou et al., 1996), Berry (Tao, Li, Li, & Gong, 2018)
77	Acetyl-ginsenoside Rg_1	***a***	$C_{44}H_{74}O_{15}$	842.502 8	Root (Chen, Balan, & Propovich, 2020), Leaf (Piao et al., 2020), RG (Xu et al., 2016b)
78	Acetyl-ginsenoside Re	***a***	$C_{50}H_{84}O_{19}$	988.560 7	Root (Chen, Balan, & Propovich, 2020), Leaf (Piao et al., 2020)
79	Malonyl-ginsenoside Rg_1	***a***	$C_{45}H_{74}O_{17}$	886.492 6	Root (Chen, Balan, & Propovich, 2020), Leaf (Piao et al., 2020), Flower (Li et al., 2017b)
80	Malonyl-ginsenoside Re	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Root (Chen, Balan, & Propovich, 2020), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), Seed (Zheng, Lei, Wang, Feng, & Wang, 2019)
81	Notoginsenoside R_1	***a***	$C_{47}H_{80}O_{18}$	932.534 5	Root and Berry (Lee et al., 2017a), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), RG (Zhou, Xu, & Yang, 2016), BG (Wang et al., 2023c)
82	Notoginsenoside R_2	***a***	$C_{41}H_{70}O_{13}$	770.481 6	Root and Leaf (Piao et al., 2020), Berry (Lee et al., 2017a), RG (Zhou, Xu, & Yang, 2016), BG (Qi et al, 2023)
83	20(*R*)-notoginsenoside R_2	***a***	$C_{41}H_{70}O_{13}$	770.481 6	Root (Piao et al., 2020), RG (Zhou et al., 2023), BG (Lee et al., 2018)
84	Notoginsenoside R_3	***a***	$C_{41}H_{70}O_{13}$	770.481 6	Stem and Leaf (Wang et al., 2023a), Berry (Lee, Seo, Singh, Lee, & Lee, 2020)
85	Notoginsenoside Rt	***a***	$C_{44}H_{74}O_{15}$	842.502 8	Root (Niu, Luo, Lyu, & Lu, 2021)
86	Koryoginsenoside R_1	***a***	$C_{46}H_{76}O_{15}$	868.518 4	Root (Wang, Zhang, Yang, Kim, & Wang, 2016)
87	Pseudoginsenoside Rt_3	***a***	$C_{42}H_{70}O_{13}$	782.481 6	Root (Lee, Lee, Yang, Kim, & Lee, 2015)
88	Chikusetsusaponin LM_1	***a***	$C_{41}H_{70}O_{12}$	754.486 7	Stem (Wang et al., 2023b), Berry (Tao, Li, Li, & Gong, 2018)
89	Ginsenoside Rh_5	***a***	$C_{37}H_{64}O_9$	652.455 0	Root (Zhu, 2020), Leaf (Dou et al., 2001), Flower (Li, Xu, Li, Cao, & Gong, 2019), Berry (Tao, Li, Li, & Gong, 2018)
90	Saponin IIb	***a***	$C_{36}H_{62}O_9$	638.439 4	Leaf (Piao et al., 2020)
91	Saponin IIIc	***a***	$C_{37}H_{62}O_{10}$	666.434 3	Leaf (Piao et al., 2020)
92	Floralginsenoside M	***a***	$C_{53}H_{90}O_{22}$	1 078.592 4	Leaf (Li & Yang, 2012), Flower (Yoshikawa, Sugimoto, Nakamura, Sakumae, & Matsuda, 2007)
93	Floralginsenoside N	***a***	$C_{53}H_{90}O_{22}$	1 078.592 4	Leaf (Li & Yang, 2012), Flower (Yoshikawa, Sugimoto, Nakamura, Sakumae, & Matsuda, 2007)
94	Floralginsenoside P	***a***	$C_{53}H_{90}O_{23}$	1 094.587 3	Flower (Yoshikawa, Sugimoto, Nakamura, Sakumae, & Matsuda, 2007)
95	Malonyl-floralginsenoside Re_2	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Flower (Qiu et al., 2017)
96	Malonyl-floralginsenoside Re_3	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Flower (Qiu et al., 2017)
97	Vinaginsenoside R_4	***a***	$C_{48}H_{82}O_{19}$	962.545 0	Root and Berry (Lee et al., 2017a), Leaf (Piao et al., 2020), Flower (Li & Gong, 2019), RG (Zhou et al., 2023), BG (Wang et al., 2023c)
98	20(*R*)-ginsenoside Rh_5	***a***	$C_{37}H_{64}O_9$	652.455 0	Flower (Li, Xu, Li, Cao, & Gong, 2019)
99	20(*S*)-methoxyl-ginsenoside Rg_3	***a***	$C_{43}H_{74}O_{13}$	798.511 9	Flower (Li et al., 2017a)
100	20(*R*)-methoxyl-ginsenoside Rg_3	***a***	$C_{43}H_{74}O_{13}$	798.511 9	Flower (Li et al., 2017a)
101	Notoginsenoside Q	***a***	$C_{63}H_{106}O_{30}$	1 342.676 9	RG (Xu et al., 2016b)
102	Vinaginsenoside R_3	***a***	$C_{48}H_{82}O_{17}$	930.555 2	Flower (Li & Gong, 2019)
103	6'-malonyl methyl ester ginsenoside F_1	***a***	$C_{40}H_{66}O_{12}$	738.455 4	Flower (Li, Li, Xu, & Gong, 2020)
104	Quinquenoside I	***a***	$C_{52}H_{86}O_{19}$	1 014.576 3	Flower (Li & Gong, 2019)
105	Malonyl-floralginsenoside Re_1	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Flower (Qiu et al., 2017)
106	Malonyl-floralginsenoside Rb_1	***a***	$C_{57}H_{94}O_{26}$	1 194.603 3	Flower (Qiu et al., 2017)
107	Malonyl-floralginsenoside Rb_2	***a***	$C_{57}H_{94}O_{26}$	1 194.603 3	Flower (Qiu et al., 2017)
108	Malonyl-floralginsenoside Rd_1	***a***	$C_{51}H_{84}O_{21}$	1 032.550 5	Flower (Qiu et al., 2017)
109	Malonyl-floralginsenoside Rc_1	***a***	$C_{56}H_{92}O_{25}$	1 164.592 8	Flower (Qiu et al., 2017)

Table 1 (*continued*)

No.	Compounds	Subtype	Formula	Accurate molecular mass	References
110	Pseudoginsenoside Rs_1	***a***	$C_{50}H_{84}O_{19}$	988.560 7	Flower (Shi et al., 2020)
111	6'-Acetyl-ginsenoside F_1	***a***	$C_{38}H_{64}O_{10}$	680.449 9	Flower (Shi et al., 2020)
112	20(*R*)-ginsenoside Rg_1	***a***	$C_{42}H_{72}O_{14}$	800.492 2	Flower (Xu, Li, Chen, & Gong, 2016)
113	Quinquenoside R_1	***a***	$C_{56}H_{94}O_{24}$	1 150.613 5	Root (Wang et al., 2023b), Stem (Wang et al., 2023a), RG (Xu et al., 2016b), BG (Wang et al., 2023c)
114	3β-acetoxyl ginsenoside F_1	***a***	$C_{38}H_{64}O_{10}$	680.449 9	Flower (Li, Li, Xu, & Gong, 2020)
115	Ginsenoside Rh_{24}	***a***	$C_{36}H_{58}O_8$	618.413 2	Flower (Li, Li, Xu, & Gong, 2020)
116	Ginsenoside Rh_{25}	***a***	$C_{52}H_{88}O_{21}$	1 048.581 8	Flower (Li, Li, Xu, & Gong, 2020)
117	Ginsenoside Rh_{26}	***a***	$C_{52}H_{86}O_{19}$	1 014.576 3	Flower (Li, Li, Xu, & Gong, 2020)
118	Notoginsenoside N	***a***	$C_{48}H_{82}O_{19}$	962.545 0	Root (Yang et al., 2012), Stem (Gong et al., 2023), Flower (Shi et al., 2020)
119	Yesanchinoside F	***a***	$C_{56}H_{94}O_{24}$	1 150.613 5	Stem and Leaf (Gong et al., 2023)
120	Vinaginsenoside R_{16}	***a***	$C_{47}H_{80}O_{17}$	916.539 6	Stem (Gong et al., 2023), Flower (Shi et al., 2020)
121	Quinquenoside L_{14}	***a***	$C_{47}H_{80}O_{17}$	916.539 6	Stem (Xue, Wang, Yu, Guo, & Wang, 2021)
122	Ginsenoside RA_0	***a***	$C_{60}H_{102}O_{28}$	1 270.655 8	Stem and Leaf (Xue, Wang, Yu, Guo, & Wang, 2021), RG (Zhang, Zhang, Li, Li, & Jia , 2022)
123	Quinquenoside L_{17}	***a***	$C_{47}H_{80}O_{18}$	932.534 5	Stem and Leaf (Xue, Wang, Yu, Guo, & Wang, 2021)
124	Notoginsenoside R_4	***a***	$C_{59}H_{100}O_{27}$	1 240.645 2	Root (Lee et al., 2017a), RG (Matsuura et al., 1984)
125	Quinquenoside F_6	***a***	$C_{47}H_{80}O_{18}$	932.534 5	Root (Chen, Balan, & Propovich, 2020)
126	Pseudoginsenoside F_8	***a***	$C_{55}H_{92}O_{23}$	1 120.602 9	Root (Pan et al., 2021)
127	Quinquenoside III	***a***	$C_{50}H_{84}O_{19}$	988.560 7	Root (Pan et al., 2021), RG (Xu et al., 2016b)
128	Yesanchinoside D	***a***	$C_{44}H_{74}O_{15}$	842.502 8	Root (Wang et al., 2016)
129	Malonyl-ginsenoside Ra_1	***a***	$C_{61}H_{100}O_{29}$	1 296.635 0	Root (Chen, Balan, & Propovich, 2020)
130	Malonyl-ginsenoside Ra_2	***a***	$C_{61}H_{100}O_{29}$	1 296.635 0	Root (Chen, Balan, & Propovich, 2020)
131	20(*R*)-Ginsenoside Rh_{19}	***a***	$C_{36}H_{62}O_9$	638.439 4	Leaf (Ma & Yang, 2016)
132	Notoginsenoside K	***a***	$C_{48}H_{82}O_{18}$	946.550 1	Root (Yang et al., 2012)
133	Ginsenjilinol	***a***	$C_{42}H_{72}O_{15}$	816.487 1	Root (Chen, Balan, & Popovich, 2020)
134	Panajaponol A	***a***	$C_{42}H_{72}O_{15}$	816.487 1	Root (Chan et al., 2011)
135	Ginsenoside Rg_{18}	***a***	$C_{48}H_{82}O_{18}$	946.550 1	Root (Lee, Lee, Kim, Cho, & Lee, 2015)
136	6-Acetyl ginsenoside-Rg_3	***a***	$C_{50}H_{84}O_{20}$	1 004.555 6	Root (Lee, Lee, Kim, Cho, & Lee, 2015)
137	Ginsenoside Rs_{11}	***a***	$C_{55}H_{92}O_{23}$	1 120.602 9	Root (Lee, Lee, Kim, Cho, & Lee, 2015)
138	Ginsenoside Rm_4	***a***	$C_{45}H_{74}O_{16}$	870.497 7	Root (Zhu, 2020)
139	Yesanchinoside E	***a***	$C_{54}H_{92}O_{23}$	1 108.602 9	Root (Zhu, 2020)
140	Notoginsenoside FP_1	***a***	$C_{47}H_{80}O_{18}$	932.534 5	Root (Zuo, Li, Li, & Yang, 2020)
141	Ginsenoside Re_5	***a***	$C_{42}H_{72}O_{15}$	816.487 1	Root (Wang et al., 2013)
142	Ginsenoside Ki	***a***	$C_{36}H_{62}O_{10}$	654.434 3	Root (Chen, Balan, & Popovich, 2020), Leaf (Piao et al., 2020)
143	Ginsenoside Km	***a***	$C_{36}H_{62}O_{10}$	654.434 3	Root (Chen, Balan, & Popovich, 2020), Leaf (Piao et al., 2020)
144	12β,25-dihydroxydammar-20 (22) *E*-ene-3-*O*-β-*D*-glucopyranosyl-(1→2)-*O*-β-*D*-glucopyranoside	***b***	$C_{42}H_{72}O_{13}$	784.497 3	RG (Zhou, Xu, & Yang, 2016)
145	25(OH)-ginsenoside Rg_5	***b***	$C_{42}H_{72}O_{13}$	784.497 3	RG (Lee, 2020)
146	Pseudo-ginsenoside Rg_2	***b***	$C_{42}H_{72}O_{13}$	784.497 3	BG (Wang et al., 2023c)
147	Ginsenoside Rh_{10}	***b***	$C_{36}H_{62}O_8$	622.444 5	Root (Lv, & Lu, 2021), RG (Cho et al., 2013)
148	Notoginsenoside B_1	***b***	$C_{36}H_{62}O_9$	638.439 4	BG (Zhao, Dou, Qu, & Zhang, 2024)
149	25(OH)-ginsenoside Rz_1	***c***	$C_{42}H_{72}O_{13}$	784.497 3	RG (Lee, 2020)
150	Ginsenoside Rg_8	***d***	$C_{42}H_{70}O_{14}$	798.476 6	Root (Zhu, 2020), Stem and Leaf (Yang et al., 2019), BG (Qi et al., 2023)
151	Ginsenoside Rg_{11}	***d***	$C_{42}H_{70}O_{14}$	798.476 6	RG (Cho et al., 2013)
152	Notoginsenoside SP_9	***e***	$C_{37}H_{64}O_{11}$	684.444 9	BG (Zhao, Dou, Qu, & Zhang, 2024)
153	Ginsenoside Re_7	***f***	$C_{50}H_{84}O_{20}$	1 004.555 6	Root (Lee, Lee, Kim, Cho, & Lee, 2015)
154	Koryoginsenoside R_2	***f***	$C_{54}H_{92}O_{24}$	1 124.597 9	Root (Dou, Hou, & Chen, 1998)
155	Ginsenoside Rg_{12}	***f***	$C_{42}H_{72}O_{15}$	816.487 1	Root (Lee et al., 2017b)
156	Ginsenoside Rm_3	***f***	$C_{42}H_{72}O_{14}$	800.492 2	Root (Zhu, 2020)
157	(3β,12β,22*E*)-Dammar-22-ene-3,12,20,25-tetrol	***f***	$C_{30}H_{52}O_4$	476.386 6	Root (Zhu, 2020)
158	Vinaginsenoside R_8	***g***	$C_{48}H_{82}O_{19}$	962.545 0	Root (Zhu, 2020), Flower (Li & Gong, 2019), Berry (Tao, Li, Li, & Gong, 2018), RG and BG (Wang et al., 2023c)
159	Majoroside F_6	***g***	$C_{48}H_{82}O_{19}$	962.545 0	Root (Lee, Lee, Yang, Kim, & Lee, 2015)
160	Ginsenoside ST_2	***g***	$C_{36}H_{62}O_{10}$	654.434 3	Root (Chen, Balan, & Propovich, 2020), Leaf (Shin, Kwon,& Park, 2015)

(*continued on next page*)

Table 1 (continued)

No.	Compounds	Subtype	Formula	Accurate molecular mass	References
161	Notoginsenoside A	***g***	$C_{54}H_{92}O_{24}$	1 124.597 9	Root (Yang et al., 2012)
162	Notoginsenoside E	***g***	$C_{48}H_{82}O_{20}$	978.539 9	Flower (Li & Gong, 2019)
163	Ginsenoside Rh_6	***g***	$C_{36}H_{62}O_{11}$	670.429 2	Leaf (Shin, Kwon, & Park, 2015), Flower (Li & Gong, 2019), Berry (Tao, Li, Li, & Gong, 2018)
164	Floralginsenoside I	***g***	$C_{48}H_{82}O_{20}$	978.539 9	Flower (Nakamura, Sugimoto, Matsuda, & Yoshikawa, 2007)
165	Floralginsenoside E	***g***	$C_{42}H_{72}O_{15}$	816.487 1	Flower (Yoshikawa, Sugimoto, Nakamura, & Matsuda, 2007)
166	Floralginsenoside F	***g***	$C_{42}H_{72}O_{15}$	816.487 1	Flower (Shi et al., 2020)
167	Floralginsenoside G	***g***	$C_{50}H_{84}O_{21}$	1 020.550 5	Flower (Shi et al., 2020)
168	Floralginsenoside K	***g***	$C_{48}H_{82}O_{21}$	994.534 9	Flower (Nakamura, Sugimoto, Matsuda, & Yoshikawa, 2007)
169	Floralginsenoside O	***g***	$C_{53}H_{90}O_{24}$	1 110.582 2	Flower (Yoshikawa, Sugimoto, Nakamura, Sakumae, & Matsuda, 2007)
170	Floralginsenoside B	***g***	$C_{42}H_{72}O_{16}$	832.482 0	Flower (Shi et al., 2020)
171	Floralginsenoside D	***g***	$C_{41}H_{70}O_{15}$	802.471 5	Flower (Yoshikawa, Sugimoto, Nakamura, & Matsuda, 2007)
172	Floralginsenoside A	***h***	$C_{42}H_{72}O_{16}$	832.482 0	Flower (Shi et al., 2020), Berry (Lee, Lee, Jeong, Byun, & Kim, 2017)
173	Majoroside F_1	***h***	$C_{48}H_{82}O_{19}$	962.545 0	Root (Zhu, 2020), Flower (Tung et al., 2010)
174	Ginsenoside Rg_7	***h***	$C_{42}H_{72}O_{14}$	800.492 2	Leaf (Shin, Kwon, & Park, 2015)
175	Ginsenoside V	***h***	$C_{54}H_{92}O_{24}$	1 124.597 9	Root (Lee, Lee, Yang, Kim, & Lee, 2015)
176	Floralginsenoside La	***h***	$C_{48}H_{82}O_{19}$	962.545 0	Flower (Shi et al., 2020)
177	Floralginsenoside Lb	***h***	$C_{48}H_{82}O_{19}$	962.545 0	Flower (Nakamura, Sugimoto, Matsuda, & Yoshikawa, 2007)
178	24(*S*)-ginsenoside M_{7cd}	***h***	$C_{36}H_{62}O_{10}$	654.434 3	Flower (Li, Xu, Li, Cao, & Gong, 2019)
179	24(*R*)-ginsenoside M_{7cd}	***h***	$C_{36}H_{62}O_{10}$	654.434 3	Flower (Li, Xu, Li, Cao, & Gong, 2019)
180	Floralginsenoside H	***h***	$C_{50}H_{84}O_{21}$	1 020.550 5	Flower (Nakamura, Sugimoto, Matsuda, & Yoshikawa, 2007)
181	Floralginsenoside Tc	***h***	$C_{53}H_{90}O_{24}$	1 110.582 2	Flower (Nguyen et al., 2010)
182	Floralginsenoside Td	***h***	$C_{53}H_{90}O_{24}$	1 110.582 2	Flower (Nguyen et al., 2010)
183	Ginsenoside I	***h***	$C_{48}H_{82}O_{20}$	978.539 9	Flower (Shi et al., 2020)
184	Ginsenoside II	***h***	$C_{48}H_{82}O_{20}$	978.539 9	Flower (Shi et al., 2020)
185	Floralginsenoside C	***h***	$C_{41}H_{70}O_{15}$	802.471 5	Flower (Yoshikawa, Sugimoto, Nakamura, & Matsuda, 2007)
186	Floralginsenoside J	***h***	$C_{48}H_{82}O_{20}$	978.539 9	Flower (Nakamura, Sugimoto, Matsuda, & Yoshikawa, 2007)
187	Floralginsenoside Ka	***h***	$C_{36}H_{62}O_{11}$	670.429 2	Flower (Li, Xu, Li, Cao, & Gong, 2019)
188	Vinaginsenoside R_9	***h***	$C_{48}H_{82}O_{19}$	962.545 0	Flower (Yoshikawa, Sugimoto, Nakamura, Sakumae, & Matsuda, 2007)
189	24(*R*)-floralginsenoside Ka	***h***	$C_{36}H_{62}O_{11}$	670.429 2	Flower (Li, Xu, Li, Cao, & Gong, 2019)
190	Ginsenoside SL_1	***h***	$C_{36}H_{62}O_{11}$	670.429 2	Root (Bai et al., 2016), Leaf (Shin, Kwon, & Park, 2015)
191	Floralginsenoside Ta	***h***	$C_{36}H_{60}O_{10}$	652.418 6	Flower (Nguyen et al., 2010)
192	Ginsenoside III	***h***	$C_{48}H_{80}O_{19}$	960.529 4	Flower (Shi et al., 2020)
193	Dehydroprotopanaxatriol I	***i***	$C_{30}H_{50}O_3$	458.376 0	Root (Yang, Hu, Wu, Ye, & Guo, 2014)
194	22(*S*)-notoginsenoside Ab_1	***i***	$C_{36}H_{60}O_9$	636.423 7	BG (Zhao, Dou, Qu, & Zhang, 2024)
195	Dehydroprotopanaxadiol II	***i***	$C_{30}H_{50}O_2$	442.381 1	Root (Yang, Hu, Wu, Ye, & Guo, 2014)
196	Ginsenoside Rs_5	***i***	$C_{44}H_{72}O_{13}$	808.497 3	Root (Wang et al., 2008), RG(Zhou, Xu, & Yang, 2016), BG (Sun, Pan, & Sung, 2011)
197	22(*R*)-notoginsenoside Ab_1	***i***	$C_{36}H_{60}O_9$	636.423 7	BG (Zhao, Dou, Qu, & Zhang, 2024)
198	Ginsenoside Rg_6	***i***	$C_{42}H_{70}O_{12}$	766.486 7	Root (Zhu, 2020), and Flower (Shi et al., 2020), RG (Zhou, Xu, & Yang, 2016), BG (Qi et al., 2023)
199	Ginsenoside Rk_3	***i***	$C_{36}H_{60}O_8$	620.428 8	Root (Zhu, 2020), Stem and Leaf (Yang et al., 2019), Flower (Shi et al., 2020), RG (Zhou et al., 2023), BG (Qi et al., 2023)
200	Ginsenoside Rs_7	***i***	$C_{38}H_{62}O_9$	662.439 4	Root (Xu et al., 2016a), RG(Park et al., 2002a)
201	Ginsenoside Rk_1	***i***	$C_{42}H_{70}O_{12}$	766.486 7	Root (Zhu, 2020), Berry (Lee et al., 2017a), Leaf (Piao et al., 2020), Flower (Li & Gong, 2019), RG and BG (Li et al., 2023)
202	Ginsenoside Rg_{10}	***i***	$C_{42}H_{70}O_{13}$	782.481 6	Root (Zhu et al., 2018), RG (Lee, Seo, Oh, & Na, 2013)
203	Ginsenoside Rk_2	***i***	$C_{36}H_{60}O_7$	604.433 9	Root (Zhu, 2020), Berry (Han et al., 2018), RG (Park et al., 2002b)
204	Ginsenoside SL_3	***j***	$C_{42}H_{70}O_{14}$	798.476 6	Leaf (Shin, Kwon, & Park, 2015)
205	20(22)-*Z*-ginsenoside Rg_9	***k***	$C_{42}H_{70}O_{13}$	782.481 6	RG (Lee, Seo, Oh, & Na, 2013)
206	Ginsenoside Rz_1	***k***	$C_{42}H_{70}O_{12}$	766.486 7	Root (Zhu, 2020), RG (Zhou, Xu, & Yang, 2016)
207	20(22)-*Z*-ginsenoside Rs_4	***k***	$C_{44}H_{72}O_{13}$	808.497 3	RG (Zhou, Xu, & Yang, 2016)
208	20(22)-*Z*-ginsenoside Rh_4	***k***	$C_{36}H_{60}O_8$	620.428 8	RG (Zhou, Xu, & Yang, 2016), BG (Zhao, Dou, Qu, & Zhang, 2024)
209	Ginsenoside Rh_3	***k***	$C_{36}H_{60}O_7$	604.433 9	Root (Zhu, 2020), Berry (Han et al., 2018), RG (Zhou et al., 2023), BG (Qi et al., 2023)
210	Ginsenoside F_4	***k***	$C_{42}H_{70}O_{12}$	766.486 7	Root (Xu et al., 2016a), Leaf (Shin, Kwon, & Park, 2015), Flower (Shi et al., 2020), Berry (Lee et al., 2017a), RG (Lee et al., 2018), BG (Sun, Pan, & Sung, 2011)
211	Ginsenoside Rg_5	***l***	$C_{42}H_{70}O_{12}$	766.486 7	Root (Zhu, 2020), Flower (Li & Gong, 2019), Berry (Lee et al., 2017a), RG (Zhou, Xu, & Yang, 2016), BG (Sun, Pan, & Sung, 2011)

Table 1 (*continued*)

No.	Compounds	Subtype	Formula	Accurate molecular mass	References
212	Ginsenoside Rh4	***l***	$C_{36}H_{60}O_8$	620.428 8	Root (Zhu, 2020), Flower (Li & Gong, 2019), Berry (Tao, Li, Li, & Gong, 2018), RG (Zhou, Xu, & Yang, 2016), BG (Sun, Pan, & Sung, 2011)
213	Dehydroprotopanaxadiol I	***l***	$C_{30}H_{50}O_2$	442.381 1	Root (Yang, Hu, Wu, Ye, & Guo, 2014)
214	Ginsenoside Rs6	***l***	$C_{38}H_{62}O_9$	662.439 4	Root (Xu et al., 2016a), RG (Park et al., 2002a)
215	12-*O*-glucoginsenoside Rh4	***l***	$C_{42}H_{70}O_{13}$	782.481 6	Root (Lv, & Lu, 2021), RG(Cho et al., 2013)
216	Isoginsenoside-Rh3	***l***	$C_{36}H_{60}O_7$	604.433 9	Berry (Wang, Li, Zheng, & Yang, 2004), BG (Qi et al., 2023)
217	Dammar-(*E*)-20(22),24-diene-3*β*,6*α*,12*β*-triol	***l***	$C_{24}H_{40}O_4$	392.292 7	Leaf (Li, Yao, & Yang, 2012)
218	Dehydroprotopanaxatriol II	***l***	$C_{30}H_{50}O_3$	458.376 0	Root (Yang, Hu, Wu, Ye, & Guo, 2014)
219	Ginsenoside Rg9	***l***	$C_{42}H_{70}O_{13}$	782.481 6	Root (Dou, Hou, & Chen, 1998) and Flower (Shi et al., 2020), RG (Zhou, Xu, & Yang, 2016)
220	3*β*,12*β*-dihydroxydammar-20(22)*E*,24-diene-6-*O*-*β*-*D*-xylopyranosyl-(1→2)-*O*-*β*-*D*-glucopyranoside	***l***	$C_{41}H_{68}O_{12}$	752.471 1	RG (Zhou, Xu, & Yang, 2016)
221	Ginsenoside Rs4	***l***	$C_{44}H_{72}O_{13}$	808.497 3	Root (Wang et al., 2008), Flower (Shi et al., 2020), RG (Zhou, Xu, & Yang, 2016), BG (Sun, Pan, & Sung, 2011)
222	Ginsenoside ST1	***m***	$C_{36}H_{60}O_{10}$	652.418 6	Leaf (Shin, Kwon, & Park, 2015)
223	Ginsenoside SL2	***m***	$C_{42}H_{70}O_{14}$	798.476 6	Leaf (Shin, Kwon, & Park, 2015)
224	Ginsenoside Rm1	***n***	$C_{48}H_{80}O_{18}$	944.534 5	Root (Zhu, 2020)
225	Ginsenoside Rm2	***o***	$C_{48}H_{80}O_{18}$	944.534 5	Root (Zhu, 2020)
226	25-Hydroxyprotopanaxatriol	***p***	$C_{30}H_{54}O_5$	494.397 1	Stem and Leaf (Li & Yang, 2012), Berry (Wang et al., 2007)
227	Vinaginsenoside R15	***p***	$C_{42}H_{72}O_{15}$	816.487 1	Root (Zhu, 2020), Flower (Shi et al., 2020)
228	Ginsenoside Rf2	***p***	$C_{42}H_{74}O_{14}$	802.507 9	RG (Park, Lee, & Kim, 1998)
229	25-Hydroxyprotopanaxadiol	***p***	$C_{30}H_{54}O_4$	478.402 2	Berry (Wang et al., 2007)
230	Ginsenoside Rf3	***p***	$C_{41}H_{70}O_{13}$	770.481 6	Flower (Li et al., 2017b)
231	25-Hydroxyginsenoside Rg2	***p***	$C_{42}H_{74}O_{14}$	802.507 9	Berry (Yu & Zhao, 2004)
232	Quinquenoside F1	***p***	$C_{42}H_{74}O_{15}$	818.502 8	Root (Dou, Hou, & Chen, 1998), RG (Xu et al., 2016b)
233	25(OH)-ginsenoside Rg3	***p***	$C_{42}H_{74}O_{14}$	802.507 9	RG (Lee, 2020)
234	Floralginsenoside Tb	***q***	$C_{35}H_{62}O_{11}$	658.429 2	Flower (Nguyen et al., 2010)
235	Floralginsenoside Kb	***r***	$C_{45}H_{76}O_{19}$	920.498 1	Flower (Tung et al., 2010)
236	Floralginsenoside Kc	***r***	$C_{45}H_{76}O_{20}$	936.493 0	Flower (Tung et al., 2010)
237	Notoginsenoside ST8	***s***	$C_{32}H_{52}O_9$	580.361 1	BG (Zhao, Dou, Qu & Zhang, 2024)
238	Pseudoginsenoside F11	***t***	$C_{42}H_{72}O_{14}$	800.492 2	Root (Dou, Hou, & Chen, 1998), Stem and Leaf (Gong et al., 2023), RG and BG (Wang et al., 2023c)
239	20(*S*),25-Epoxydammarane-3*β*,12*β*,24*α*-triol	***u***	$C_{30}H_{52}O_4$	476.386 6	RG (Zheng et al., 2016)
240	20(*S*),25(*R*)-Epoxydammarane-3*β*,12*β*,24*β*,26-tetraol	***u***	$C_{30}H_{52}O_5$	492.381 5	RG (Zheng et al., 2016)
241	Ginsenoside La	***v***	$C_{42}H_{70}O_{13}$	782.481 6	Leaf (Yang et al., 2019)
242	Ginsenoside Rh22	***v***	$C_{36}H_{60}O_9$	636.423 7	Flower (Shi et al., 2020)
243	12,23-Epoxyginsenoside Rg1	***v***	$C_{42}H_{70}O_{14}$	798.476 6	Leaf (Shin, Kwon, & Park, 2015)
244	7*β*-Hydroxyl ginsenoside Rd	***w***	$C_{48}H_{82}O_{19}$	962.545 0	Flower (Li, Li, Xu, & Gong, 2020)
245	3-Keto-20(*S*)-protopanaxatriol	***x***	$C_{30}H_{50}O_4$	474.370 9	Seed (Sugimoto, Nakamura, Matsuda, Kitagawa, & Yoshikawa, 2009)
246	Ginsenoside Rh8	***y***	$C_{36}H_{60}O_9$	636.423 7	Root (Zhu, 2020), Leaf (Shin, Kwon, & Park, 2015), Flower (Li & Gong, 2019)
247	Ginsenoside Rh7	***z***	$C_{36}H_{60}O_9$	636.423 7	Root (Chen, 2021), Leaf (Shin, Kwon, & Park, 2015), RG and BG (Wang et al., 2023c)
248	Notoginsenoside G	***z***	$C_{48}H_{80}O_{19}$	960.529 4	Leaf (Gong et al., 2023)
249	5,6-Didehydro-ginsenoside Rd	***z***	$C_{48}H_{80}O_{18}$	944.534 5	Flower (Li & Gong, 2019)

RG: red ginseng; BG: black ginseng.

Table 2
Information of two saponins of lanostane type tetracyclic triterpenoid saponins.

No.	Compounds	Formula	Accurate molecular mass	References
250	Lanost-5,24-dien-3*β*-ol-3-*O*-*β*-*D*- glucopyranosyl-(6′→1″)-*D*-glucopyranosyl-(6″→1‴)-*β*-*D*-glucopyranoside	$C_{48}H_{81}O_{16}$	913.552 5	RG (Chung et al., 2014)
251	Hebevinoside VI	$C_{41}H_{68}O_{12}$	752.471 1	RG (Xu, et al., 2016b)

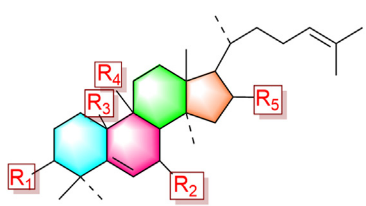
RG: red ginseng.

are also *trans* condensed rings. The ^{13}C NMR spectrum of ursane type triterpenoids differs from that of oleananes in terms of the chemical shift signals of the olefinic carbon atoms. Specifically, the δ_C of C-12 and C-13 are typically 124 and 139, respectively (Camargo et al., 2022). In addition, the number of quaternary carbon signals varies, with six signals observed in the spectrum of oleananes and five signals in the spectrum of ursanes.

A total of two (**270**–**271**) ursane type pentacyclic triterpenoid saponins were reported. They are both identified from red ginseng (Table 4, Fig. 6).

6. Spatial distribution and subtype comparison of saponins from different sources

Analyzing the distribution of saponins in various parts based on their quantity: as shown in the Venn diagram (Fig. 7), a total of 243 saponins were identified from the root, stem, leaf, flower, berry, seed parts of *P. ginseng*. Among them, a total of 147 saponins were reported in the underground part (root), and a total of 174 saponins were reported in the aerial parts (stem, leaf, flower, berry, seed). There are a total of 32 shared saponins (including 31 tetracyclic triterpenoids and one pentacyclic triterpenoid) in all the parts of ginseng. And there are 69, 18, 61 and four unique saponins in the root, stem & leaf, flower, berry & seed part, respectively. The numbers of saponins merely shared by roots & stem & leaf, root & flower, root & berry & seed, stem & leaf & flower, stem & leaf & berry & seed, flower & berry & seed were 17, nine, three, four, seven, and one, respectively.



250 R_1=O-glu^6-^{1}glu^6-^{1}glu, R_2=H, R_3=CH_3, R_4=H, R_5=H
251 R_1=O-xyl, R_2=OH, R_3=H, R_4=CH_3, R_5=O-glu

Fig. 4. Lanostane type tetracyclic triterpenoid saponins.

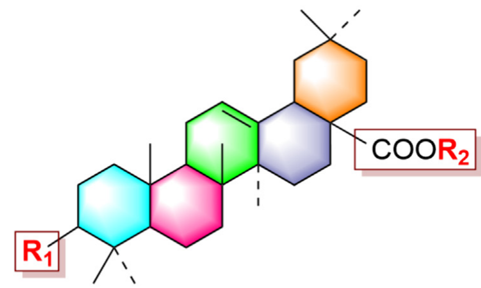
As shown in Fig. 8, a total of 103 saponins were reported in the RG, and a total of 65 saponins were reported in the BG. There are a total of 55 shared saponins (including 54 damarane type tetracyclic triterpenoids and one oleanolic acid type pentacyclic triterpenoids) in the root of *P.* ginseng, RG and BG. And there are 23 and eight unique saponins in RG and BG, respectively. The numbers of saponins shared by root & RG, root & BG, RG & BG were 24, one, and one, respectively. The roots, red ginseng and black ginseng share most of the subtypes (***a***, ***b***, ***d***, ***g***, ***i***, ***k***, ***l***, ***t***, ***z***). The unique subtypes of red ginseng are ***c*** and ***u***, the unique subtype of black ginseng is ***e*** and ***s***, while subtypes ***p*** exist in the roots and red ginseng but do not exist in black ginseng.

Quantitative analysis of ginsenoside is of great importance for ginseng studies because each ginsenoside demonstrates different activities. The *Chinese Pharmacopoeia* (2020 edition) defines that for ginseng, the total content of Re and Rg_1 is no less than 0.30%, and the content of Rb_1 is no less than 0.20% (Chinese Pharmacopeia Commission, 2020); While for red ginseng, it contains no less than

Table 3
Information of 18 saponins of oleanolic acid type pentacyclic triterpenoid saponins.

No.	Compounds	Formula	Accurate molecular mass	References
252	Oleanolic acid	$C_{30}H_{48}O_3$	456.360 3	Root (Zhu, 2020)
253	Polyacetylene ginsenoside Ro	$C_{65}H_{100}O_{21}$	1 216.675 7	Root (Zhang et al., 2002), RG (Zhou, Xu, & Yang, 2016)
254	Ginsenoside Ro methylester	$C_{49}H_{78}O_{19}$	970.513 7	Root (Zhang et al., 2002), RG (Zhou, Xu, & Yang, 2016)
255	Calenduloside B	$C_{48}H_{78}O_{18}$	942.518 8	Root (Lee, Lee, Yang, Chen, & Lee, 2015)
256	Ginsenoside Ro	$C_{48}H_{76}O_{19}$	956.498 1	Root and Berry (Lee et al., 2017a), Leaf (Piao et al., 2020), Flower (Wu, Lu, Teng, Guo, & Liu, 2016), RG (Zhou, Xu, & Yang, 2016), BG (Qi et al, 2023)
257	Ginsenoside Ro_1	$C_{54}H_{86}O_{24}$	1 118.550 9	Root (Zuo, Li, Li, & Yang, 2020)
258	Ginsenoside Ri	$C_{35}H_{56}O_7$	588.402 6	Root (Fu, Li, & Yang, 1998)
259	Ginsenoside-Ro-6′-butyl ester	$C_{53}H_{91}O_{18}$	1 015.620 5	Root (Zhu, 2020), RG (Zhou, Xu, & Yang, 2016)
260	Chikusetsusaponin IVa	$C_{42}H_{66}O_{14}$	794.445 3	Stem (Wang, et al., 2023a), Flower (Shi et al., 2020), Seed (Han et al., 2018)
261	Zingibroside R_1	$C_{42}H_{66}O_{14}$	794.445 3	Root (Chen, Balan, & Propovich, 2020), Stem (Gong et al., 2023)
262	Stipuleanoside R_1	$C_{47}H_{74}O_{18}$	926.487 5	RG (Xu et al., 2016b)
263	Spinasaponin A	$C_{42}H_{66}O_{14}$	794.445 3	RG (Xu et al., 2016b)
264	Oleanolic acid-28-*O*-*β*- *D*-glucopyranoside	$C_{36}H_{58}O_8$	618.413 2	RG (Xu et al., 2016b)
265	Chikusetsusaponin IV	$C_{47}H_{74}O_{18}$	926.487 5	Stem (Wang et al., 2023a), RG (Zhang, Zhang, Li, Li, & Jia, 2022)
266	Chikusetsusaponin IVa methyl ester	$C_{43}H_{68}O_{14}$	808.460 9	RG (Zhou, Xu, & Yang, 2016)
267	Chikusetsusaponin IVa butyl ester	$C_{46}H_{74}O_{14}$	850.507 9	RG (Zhou, Xu, & Yang, 2016)
268	Pseudoginsenoside RT_1	$C_{47}H_{74}O_{18}$	926.487 5	Stem (Wang et al., 2023a)
269	*O*-(*β*-*D*-glucopyranosyl)-oleanolic acid-28-*O*-(*β*-*D*-glucopyranosyl)	$C_{42}H_{68}O_{13}$	780.466 0	Root (Zhu, 2020)

RG: red ginseng; BG: black ginseng.



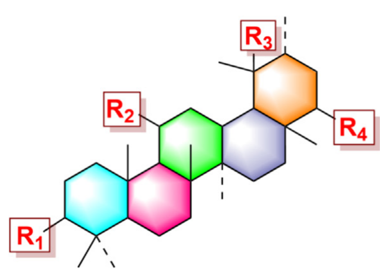
252 R_1=OH, R_2=H
253 R_1=O-(6-polyacetylene)gluA^{2}-^{1}glu, R_2=glu
254 R_1=O-(6-methyl)gluA^{2}-^{1}glu, R_2=glu
255 R_1=O-glu^{4}-^{1}glu, R_2=glu
256 R_1=O-gluA^{2}-^{1}glu, R_2=glu
257 R_1=O-gluA^{2}-^{1}glu, R_2=glu^{6}-^{1}glu
258 R_1=OH, R_2=araf
259 R_1=O-(6-butylester)gluA^{2}-^{1}glu, R_2=glu
260 R_1=O-gluA, R_2=glu
261 R_1=O-gluA^{2}-^{1}glu, R_2=H
262 R_1=O-(3-glu) gluA$^{4-1}$araf, R_2=H
263 R_1=O-gluA^{3}-^{1}glu, R_2=H
264 R_1=OH, R_2=glu
265 R_1=O-gluA^{4}-^{1}araf, R_2=glu
266 R_1=O-gluA-methyl ester, R_2=glu
267 R_1=O-gluA-butyl ester, R_2=glu
268 R_1=O-gluA^{2}-^{1}xyl, R_2=glu
269 R_1=O-glu, R_2=glu

Fig. 5. Oleanane type pentacyclic triterpenoid saponins.

Table 4
Information of two saponins of ursane type pentacyclic triterpenoid saponins.

No.	Compounds	Formula	Accurate molecular mass	References
270	Ursan-3*β*,19*α*,22*β*-triol-3-*O*-*β*- *D*-glucopyranosyl (2′→1″)-*β*-*D*- glucopyranoside	$C_{42}H_{73}O_{13}$	785.505 1	RG (Chung et al., 2014)
271	Ursan-3*α*-11*β*-diol-3-*O*-*α*- *D*-glucopyranosyl-(6′→1″)-*α*- *D*-glucopyranosyl-(6″→1‴)-*α*- *D*-glucopyranosyl- (6‴→1⁗)-*α*- *D*-glucopyranoside	$C_{54}H_{93}O_{22}$	1 093.615 9	

RG: red ginseng; BG: black ginseng.



270 R_1=O-glu^{2}-^{1}glu, R_2=H, R_3=OH, R_4=OH
271 R_1=O-glu^{6}-^{1}glu^{6}-^{1}glu^{6}-^{1}glu, R_2=OH, R_3=H, R_4=H

Fig. 6. Ursane type pentacyclic triterpenoid saponins.

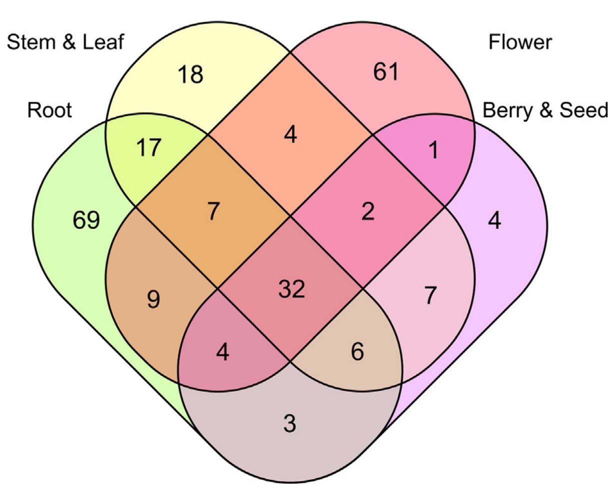


Fig. 7. Venn diagram of saponins according to different parts of *P. ginseng*.

0.20% Rb_1 and no less than 0.25% of Re and Rg_1. However, the sole control of these three ginsenosides makes it difficult to assess the distinct inherent quality between ginseng and processed ginseng. According to a simultaneous quantification research of 19 ginsenosides in white ginseng, red ginseng, and black ginseng by HPLC-ELSD (Sun et al., 2009), only Rg_1, Re, Rf, Rb_1, Rc, Rb_2, Rd, PPD, and PPT were present in white ginseng. Additionally, red ginseng also contains 20(*S*)-Rg_3, 20(*R*)-Rg_3, Rk_1, and Rg_5. Furthermore, black ginseng also comprises 20(*S*)-Rg_3, 20(*R*)-Rg_3, Rk_1, Rg_5, Rg_6, F_4, Rk_3, Rh_4, 20(*S*)-Rs_3, 20(*R*)-Rs_3, Rs_5, and Rs_4.

Analyzing the distribution of saponins in various parts based on their structure type: As shown in the pie charts (Fig. 9), the damarane type tetracyclic triterpenoid saponins are the main components. Among this type triterpenoids, the saponins (subtype *a*–*h*) with one double bond occupy the largest proportion (70.8%). The remaining subtypes (*i*–*z*) are the damarane type triterpenoid saponins with side chain changes including two double bonds, no double bond, forming a ring, a chain cleavage, alterations in the skeleton. A total of 103, 65 saponins are reported from red ginseng

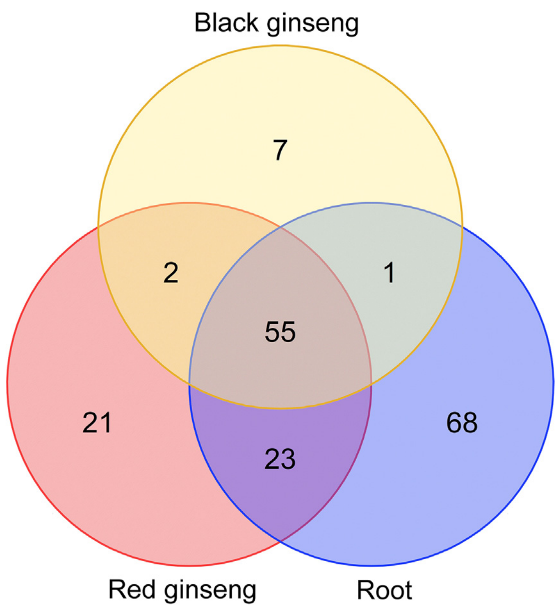


Fig. 8. Venn diagram of saponins among roots of *P.* ginseng, red ginseng and black ginseng.

and black ginseng, respectively. In addition, red ginseng (19.4%) and black ginseng (20.0%) contain more saponins with two double bonds in side chain, which were higher than the proportion of other sources (root 15.0%, stem & leaf 7.5%, flower 6.7%, berry & seed 11.9%). Besides damarane type tetracyclic triterpenoids, there are also lanostane type tetracyclic triterpenoids, oleanane type pentacyclic triterpenoids, and ursane type pentacyclic triterpenoids in ginseng and steam-processed ginseng, with oleanane type pentacyclic triterpenoids being majority.

7. Transformation

Damarmane type tetracyclic triterpenoid saponins have diverse structural types and complex side chain changes, sometimes involving changes in the skeleton of the tetracyclic ring. During the metabolism and processing of tetracyclic triterpenoid saponins, secondary ginsenosides with diverse side chains have been formed by several ways, such as hydration, dehydration, hydroxylation, oxidation, side chain cleavage, cyclization, isomerization, and double bond migration (Li, Liang, Xie, Wang, & Huang, 2024) (Fig. 10). According to the differences in the side chain structure and skeleton, we have sorted out the possible transformation relationships among damarmane type tetracyclic triterpenoid saponins. According to the alterations of the side chain and skeleton, the subtypes of the tetracyclic triterpenoids were classified into from ***a*** to ***z***. The subtype ***a*** could be regarded as derivatives of protopanaxadiol and protopanaxatriol (Huang, Li, & Wu, 2023). Hydration and dehydration often occurs during the transformation (Zhu, Luan, Dou, & Huang, 2019), including yielding subtype ***i***, ***k*** and ***l*** from subtype ***a*** by dehydration, followed by obtaining ***j*** from ***i*** via peroxidation, acquiring ***m*** from ***l*** by peroxidation and double bond migration, and getting ***n*** from ***l*** through double bond migration. Subtype ***a*** could be transformed to subtypes *b*–*h* by double bond migration, among them subtype ***b*** and ***c*** can be transformed to each other by isomerization, then subtype ***b*** could be cyclized and hydroxylated to subtype ***d***, followed by hydrolysis and methylation to yield subtype ***e***. Besides, subtype ***p*** and ***q*** do not contain double bonds, subtype ***p*** could be obtained from subtype ***a*** by hydration, and transformed to subtype ***q*** by side chain cleavage. Via side chain cleavage and oxidation, subtype ***a*** could be transformed to subtype ***r*** and ***s*** by side chain cleavage. Cyclization is also an important reaction, the hydrolysis of subtype ***a*** leads to the formation of a six-membered ring containing oxygen (subtype ***u***), a five-membered ring containing oxygen (subtype ***t***) and a seven-membered ring containing oxygen (subtype ***v***). Besides, subtype ***x*** and subtype ***y*** are yielded from subtype ***a*** by oxidation at C-3 and C-12, respectively, and subtype ***w*** is obtained from subtype ***a*** via hydroxylation at C-7.

During the steaming process of ginseng, ginsenosides undergo transformation into constituents of low polarity through hydrolysis, isomerization, and dehydration at C-20. Moreover, hydrolysis also takes place at C-3 or C-6 (Zhu, Luan, Dou, & Huang, 2019). There are two remarkable structural alterations in ginsenosides during steaming. One is that the number of sugar moieties decreases through hydrolysis. After steaming, the sugar moieties at C-20 are usually hydrolyzed first. Next, the sugar moieties at C-6 or C-3 are hydrolyzed. For instance, PPT-type ginsenosides (Re and Rg_1) initially lose their sugar residues at C-20 through degradation to form Rg_2 and Rh_1, Rh_1 can also be obtained by removing a sugar (-rha) at C-6 position of Rg_2 by hydrolysis (Huang, Li, & Wu, 2023). Similarly, PPD-type ginsenosides (Rb_1, Rb_2, Rb_3, and Rc) lose their sugar residues (-glu, -arap, and -araf) at the C-20 position through hydrolysis to form Rd, the sugar of Rd at C-20 position is hydrolyzed to obtain Rg_3, and then Rg_3 can

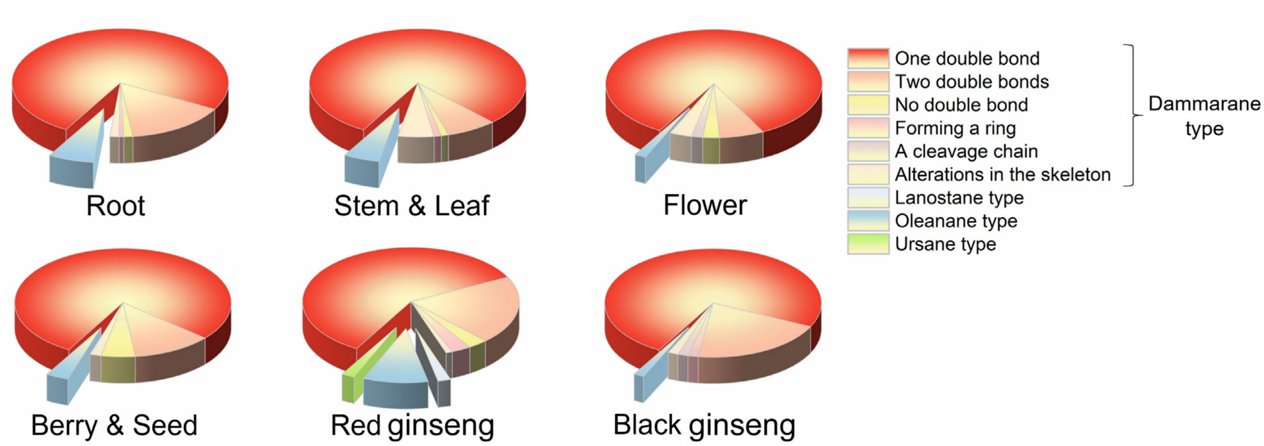


Fig. 9. Pie charts of different subtypes comparison of saponins from different sources.

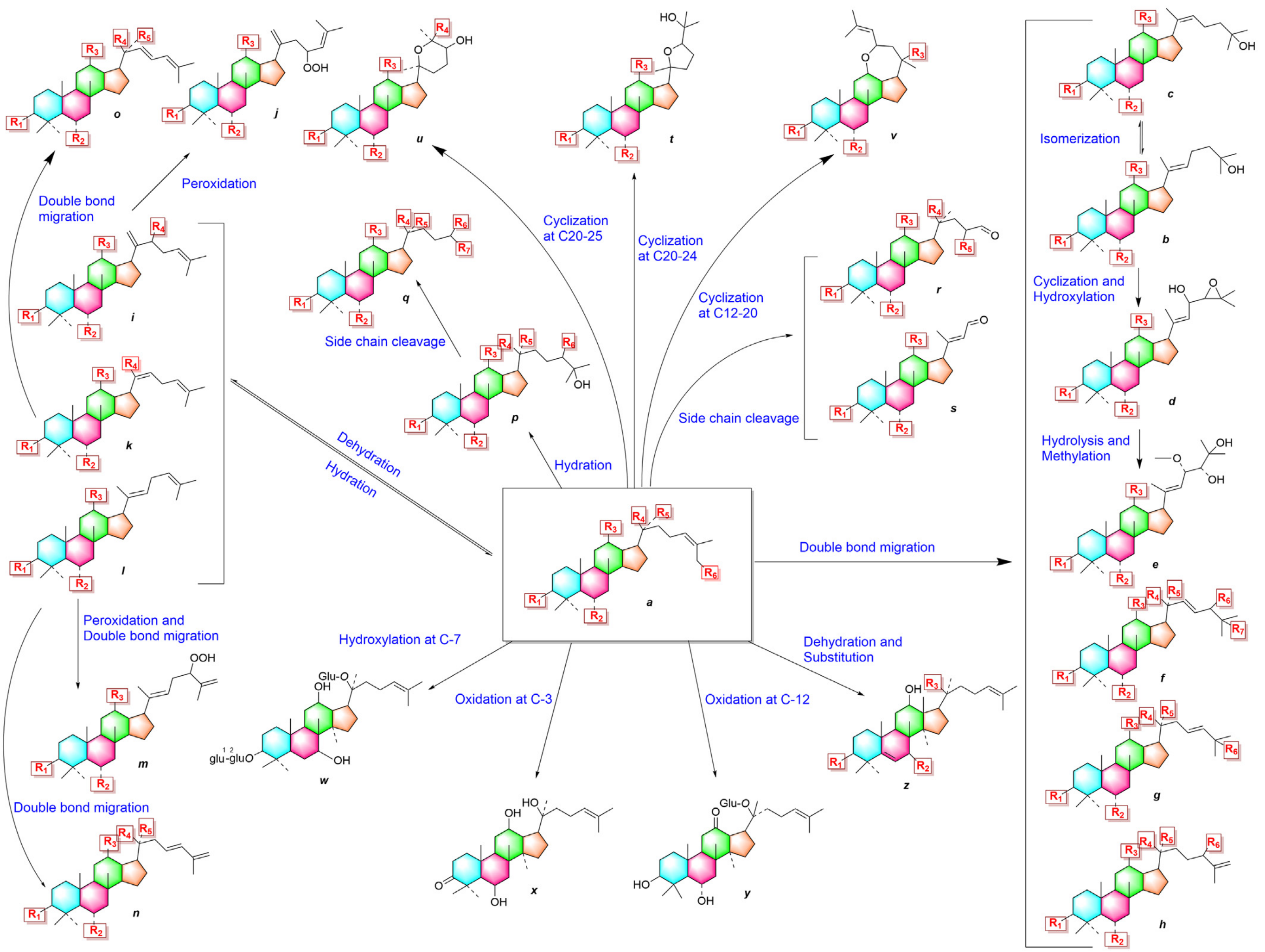


Fig. 10. Potential transformation pathway of tetracyclic triterpenoid saponins.

also lose a terminal glycogroup at C-3 to form Rh_2. Another change is that subsequent dehydration at C-20 leads to the production of geometric isomers. For example, Rg_3 is converted into two geometric isomers, Rk_1 and Rg_5, through dehydration. Rh_1 produces Rk_3 and Rh_4, and Rk_1/Rg_5 and Rk_3/Rh_4 represent a positional isomer of the double bond at C-20/21 or C-20/22 (Wang, Zhang, Zhang, & Yuan, 2024).

Pentacyclic triterpenoid saponins possess several side chain structures, and sometimes alterations occur in the pentacyclic skeleton. During the metabolism and processing of pentacyclic triterpenoid saponins, ginsenosides with various side chain structures are generated through multiple approaches, such as hydrolysis (Fan et al., 2024), dehydration, and isomerization, the possible transformation relationships between pentacyclic triterpenoid saponins were sorted out in Fig. 11. Compounds **253**, **254** and **259** are hydrolyzed at C-3 to produce **256**. In addition, compound **257** can also have a sugar (-glu) removed at C-28 position through hydrolysis to produce **256**, and is subsequently further hydrolyzed at C-28 to yield **261**. Compounds **263** and **261** are isomers of each other. Compounds **256**, **265**, **266**, **267** and **268** undergo hydrolysis at C-3 position to produce compound **260**. Furthermore, compound **255** is initially hydrolyzed at C-3 to obtain compound **269**, which can be further hydrolyzed at C-3 to generate compound **264**. Compound **264** is subsequently hydrolyzed at C-28 to remove a sugar (-glu), thereby forming compound **252**. Compound **252** could also be obtained by eliminating a sugar (-araf) at C-28 from compound **258**.

8. Conclusion

ginseng possesses valuable medicinal significance and has been extensively investigated because of its wide-ranging application in clinical therapy, healthcare products, as well as in foods and food additives throughout the world. *P. ginseng* is known to contain abundant amounts of chemical composition, especially for saponins. This review updates the ginsenosides list up to 271 from *P. ginseng* and the steam-processed ginseng (red ginseng and black ginseng) by June of 2024. Overall, we have comprehensively summarized the information regarding structural characteristics, spatial distribution, comparisons of different subtypes from various sources, processed products, and transformation, which facilitates more profound research on ginsenosides and contributes to the future development of ginseng.

However, there are still some challenges for ginseng research. In recent years, many researchers have focused on the treatment of diseases with ginsenosides, including tumor diseases, fibrosis diseases, inflammatory diseases, neurological diseases, immune diseases, cardiovascular and cerebrovascular diseases, *etc.* Ginsenosides showed significant therapeutic efficacy and few

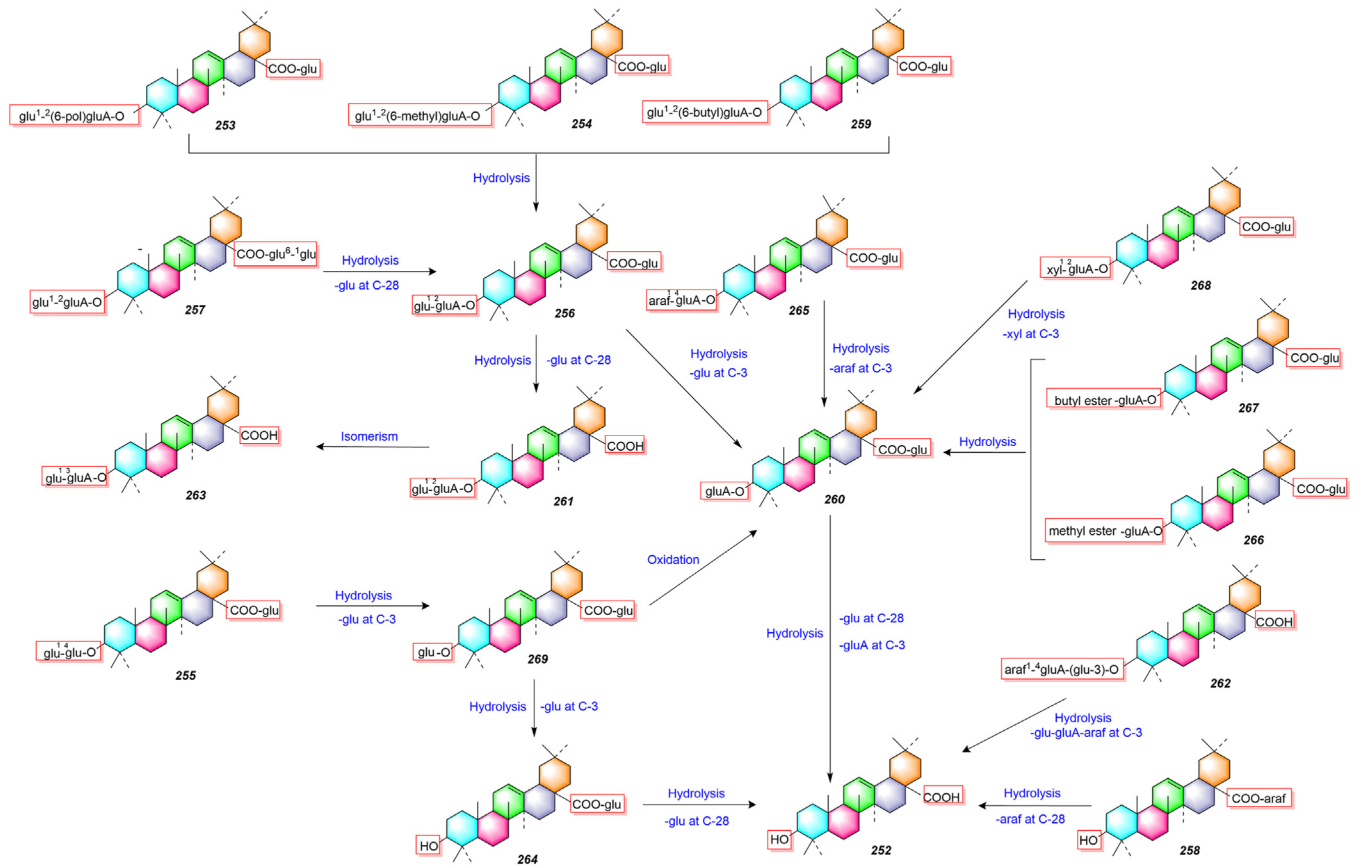


Fig. 11. Potential transformation pathway of pentacyclic triterpenoid saponins.

adverse reactions, but there are presently few clinical drugs and further development is necessary. And further in-depth studies on the mechanism of ginsenosides in treating diseases are required, with the aim of obtaining more definite targets and developing them into drugs more successfully. What' s more, the transformation of ginsenosides into rare ginsenosides is very meaningful and promising. Therefore, in the future, some efforts might be concentrated on developing more efficient, green, economic and standardized synthesis conditions, facilitating the industrial production of more rare ginsenosides.

CRediT authorship contribution statement

Xiaoyu Geng: Data curation, Formal analysis, Visualization, Writing – original draft. **Jia Wang:** Data curation, Visualization. **Yuwei Liu:** Data curation, Visualization. **Linxuan Liu:** Data curation, Formal analysis. **Xuekun Liu:** Writing – review & editing. **Yan Zhao:** Writing – review & editing. **Cuizhu Wang:** Data curation, Supervision, Writing – original draft, Writing – review & editing. **Jinping Liu:** Conceptualization, Project administration, Validation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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