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Chemotaxonomic study of the genus *Paris* based on steroidal saponins

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A B S T R A C T

The study of saponins from the genus *Paris* (Trilliaceae) has led to the isolation of over 70 steroidal saponins. Their distributions in different species are summarised and possible patterns in the modifications of the aglycone moiety, based on a biosynthetic pathway for steroidal saponins, were reviewed in this study. The chemotaxonomic value of these secondary metabolites has been evaluated, and it is suggested that *Paris thibetica*, *Paris vietnamensis*, *Paris delavayi* and *Paris pseudothibetica*, which contain more active saponins, could be an ideal substitution material for *Paris polyphylla* Smith var. *chinensis*, and *Paris polyphylla* Smith var. *yunnanensis*. Distribution of the same types of saponins amongst the Trilliaceae suggests a close relationship between the *Trillium* and *Paris*.

1. Introduction

The genus *Paris* (Trilliaceae) consists of 24 plant species and is widely distributed in the tropical and temperate regions of Europe and Asia. There are 19 species of *Paris* grown in southwest China, and many of these species have long been used to treat fractures, parotitis and hemostasis in traditional Chinese medicine (Li, 1998). Steroidal saponins are the main components in *Paris polyphylla* (Zhang, 2007). Species that have been previously investigated are listed together with their steroidal saponin content in Table 1. However, the delimitation of the genus and its subdivisions are unresolved questions in the taxonomy of *Paris* (Ji et al., 2006), largely because of the similar habitats and characteristics of the plant (Li, 1998). A chemotaxonomic investigation of the genus *Paris* was published by Chen et al. (1987) and Huang et al. (2005a). Since 1987, a large number of additional steroidal saponins from the genus *Paris* have been discovered (Huang et al., 2005a, 2007; Zhao et al., 2007; Zhang et al., 2009). On the basis of these data, we would like to re-investigate the genus *Paris* through the lens of chemotaxonomy, with particular emphasis on the relationship between *Trillium* and *Paris* in light of chemical evidence.

In this paper, chemical and biological information on saponins, obtained from different *Paris* species, is collated to (i) speculate on possible patterns resulting from modifications in the aglycone moiety based on a biosynthetic pathway for saponins and (ii) review the kinds of sugar units and linkage positions of sugar moiety connected with their aglycone. The correlations between the chemical compositions and the morphology could lead to new taxonomic conclusions.

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Table 1
Saponins from *Paris* species.

Species	No.	Saponins	Ref.
P. polyphylla Smith		**1–8, 11, 13–15, 18, 20–22, 24, 27, 44, 46, 56, 64**	Huang et al., 2009b
	1	Diosgenin-3-*O*-*β*-D-glc (Trillin)	Seshadri et al., 1972
	2	Diosgenin-3-*O*-*α*-L-rha-(1 → 4)-*β*-D-glc	Seshadri et al., 1972
	3	Diosgenin-3-*O*-*α*-L-rha-(1 → 2)-*β*-D-glc (Paris V)	Mimaki et al., 1999
	4	Diosgenin-3-*O*-*α*-L-rha-(1 → 3)-*β*-D-glc (Polyphyllin C)	Singh et al., 1982a
	5	Diosgenin-3-*O*-*α*-L-ara-(1 → 4)-*β*-D-glc	Miyamura et al., 1982
	6	Diosgenin-3-*O*-*α*-L-rha-(1 → 2)-[*α*-L-ara-(1 → 4)]-*β*-D-glc (Polyphyllin D/Paris I)	Mimaki et al., 1999
	7	Diosgenin-3-*O*-*α*-L-rha-(1 → 2)-[*α*-L-rha-(1 → 4)]-*β*-D-glc (Dioscin/Paris III)	Chen et al., 1987
	8	Diosgenin-3-*O*-*α*-L-ara-(1 → 4)-[*α*-L-rha-(1 → 3)]-*β*-D-glc	Singh et al., 1982a
	11	Diosgenin-3-*O*-*α*-L-rha-(1 → 4)-[*α*-L-ara-(1 → 3)]-*β*-D-glc	Seshadri and Vydeeswaran, 1972
	13	Diosgenin-3-*O*-*α*-L-rha-(1 → 4)-*α*-L-rha-(1 → 3)-[*β*-D-glc-(1 → 2)]-*α*-L-rha (Polyphyllin F)	Singh et al., 1982a
	14	Diosgenin-3-*O*-*α*-L-rha-(1 → 2)-*α*-L-rha-(1 → 4)-[*α*-L-rha-(1 → 3)]-*β*-D-glc (Polyphyllin E)	Singh et al., 1982a
	15	Diosgenin-3-*O*-*β*-D-glc-(1 → 3)-*α*-L-rha-(1 → 4)-[*α*-L-rha-(1 → 3)]-*β*-D-glc	Indresh et al., 1975
	18	Pennogenin-3-*O*-*β*-D-glc	Mimaki et al., 1999
	20	Pennogenin-3-*O*-*α*-L-ara-(1 → 4)-*β*-D-glc	Miyamura et al., 1982
	21	Pennogenin-3-*O*-*α*-L-rha-(1 → 2)-[*α*-L-ara-(1 → 4)]-*β*-D-glc (Paris-H)	Mimaki et al., 1999
	22	Pennogenin-3-*O*-*α*-L-rha-(1 → 2)-[*β*-D-glc-(1 → 3)]-*β*-D-glc (Paris D)	Mimaki et al., 1999
	24	Pennogenin-3-*O*-*α*-L-rha-(1 → 4)-*α*-L-rha-(1 → 4)-*β*-D-glc	Mimaki et al., 1999
	27	Pennogenin-33-*O*-{*O*-*α*-L-rha-(1 → 2)-*O*-[*O*-*β*-xyl-(1 → 5)-*α*-L-ara-(1 → 4)]-*β*-D-glucopyranoside	Deng et al., 2008
	44	(25*R*)-26-*O*-*β*-D-glc-22-hydroxy-5-ene-furost-3*β*,26-diol-3-*O*-*α*-L-rha-(1 → 3)-[*α*-L-ara-(1 → 4)]-*β*-D-glc (Polyphyllins G)	Singh et al., 1982b
	46	(25*R*)-26-*O*-*β*-D-glc-22-methoxy-5-ene-furost-3*β*,26-diol-3-*O*-*α*-L-rha-(1 → 3)-[*α*-L-ara-(1 → 4)]-*β*-D-glc (Polyphyllins H)	Singh et al., 1982b
	56	pregna-5,16-diene-3-ol-20-one-3-*O*-*α*-L-rha-(1 → 2)-[*α*-L-rha-(1 → 4)]-*β*-D-glc	Seshadri et al., 1972
	64	26-*O*-*β*-D-glc-(25*R*)-$^{\triangle(5.6),(17.20)}$-dien-16,22-dione-cholestan-3*β*,26-diol-3-*O*-*α*-L-ara-(1 → 4)-[*α*-L-rha-(1 → 2)]-*β*-D-glc	Zhao et al., 2007
PPY		**1–8, 10, 14–17, 19–21, 23, 25, 26, 32–39, 41, 42, 45, 48, 49, 53, 54, 59–61, 67, 68, 70–72**	Huang et al., 2009b
	10	Diosgenin-3-*O*-*α*-L-rha-(1 → 2)-[*β*-D-glc-(1 → 3)]-*β*-D-glc (Gracillin)	Kang et al., 1995
	16	Diosgenin-3-*O*-*α*-L-rha-(1 → 5)-*α*-L-ara-(1 → 4)-[*α*-L-rha-(1 → 2)]-*β*-D-glc (Reclinatoside)	Zhao, 2007
	17	Diosgenin-3-*O*-*β*-D-glc-(1 → 5)-*α*-L-ara-(1 → 4)-[*α*-L-rha-(1 → 2)]-*β*-D-glc (Loureiroside)	Zhao, 2007
	19	Pennogenin-3-*O*-*α*-L-rha-(1 → 2)-*β*-D-glc (Paris-VI)	Chen et al., 1983a
	23	Pennogenin-3-*O*-*α*-L-rha-(1 → 2)-[*α*-L-rha-(1 → 4)]-*β*-D-glc	Chen et al., 1990a
	25	Pennogenin-3-*O*-*α*-L-rha-(1 → 4)-*α*-L-rha-(1 → 4)-[*α*-L-rha-(1 → 2)]-*β*-D-glc (Paris-VII or Tg)	Chen et al., 1990b
	26	Pennogenin-3-*O*-*α*-L-rha-(1 → 4)-*α*-L-rha-(1 → 3)-[*α*-L-rha-(1 → 2)]-*β*-D-glc (Polyphylloside)	Matsuda et al., 2003
	32	27-hydroxyl-pennogenin	Chen and Zhou, 1992
	33	27-hydroxyl-pennogenin-3-*O*-*α*-L-rha-(1 → 4)-*α*-rha-(1 → 4)-[*α*-L-rha-(1 → 2)]-*β*-D-glc (Polyphylloside III)	Chen et al., 1995a
	34	23,27-dihydroxyl-pennogenin	Chen and Zhou, 1992
	35	23,27-dihydroxyl-pennogenin-3-*O*-*α*-L-rha-(1 → 4)-*α*-L-rha-(1 → 4)-[*α*-L-rha-(1 → 2)]-*β*-D-glc (Polyphylloside IV)	Chen et al., 1995a
	36	(25*R*)-spirost-5-en-3*β*,7*β*-diol-3-*O*-*α*-L-ara-(1 → 4)-[a-L-rha-(1 → 2)]-*β*-D-glc (Parisyunnanoside D)	Zhao, 2007
	37	(25*R*)-spirost-5-en-3*β*,7*α*-diol-3-*O*-*α*-L-ara-(1 → 4)-[a-L-rha-(1 → 2)]-*β*-D-glc (Parisyunnanoside E)	Zhao, 2007
	38	(25*R*)-spirost-5-ene-3*β*,12*α*-diol-3-*O*-*α*-L-rha-(1 → 4)-*α*-L-rha-(1 → 4)-[*α*-L-rha-(1 → 2)]-*β*-D-glc (Parisyunnanoside C)	Zhao et al., 2007
	39	(23*S*,25*S*)-3*β*,23,27-trihydroxyspirost-5-en-3-*O*-*β*-D-glc-(1 → 6)-*β*-D-glc	Liu et al., 2006c
	41	(25*R*)-26-*O*-*β*-D-glc-22-hydroxy-5-ene-furost-3*β*,26-diol-3-*O*-*α*-L-rha-(1 → 2)-[*α*-L-ara-(1 → 4)]-*β*-D-glc (Parisaponin I)	Matsuda et al., 2003
	42	(25*R*)-26-*O*-*β*-D-glc-22-hydroxy-5-ene-furost-3*β*,26-diol-3-*O*-*α*-L-rha-(1 → 2)-[*β*-D-glc-(1 → 3)]-*β*-D-glc (Protogracillin)	Matsuda et al., 2003