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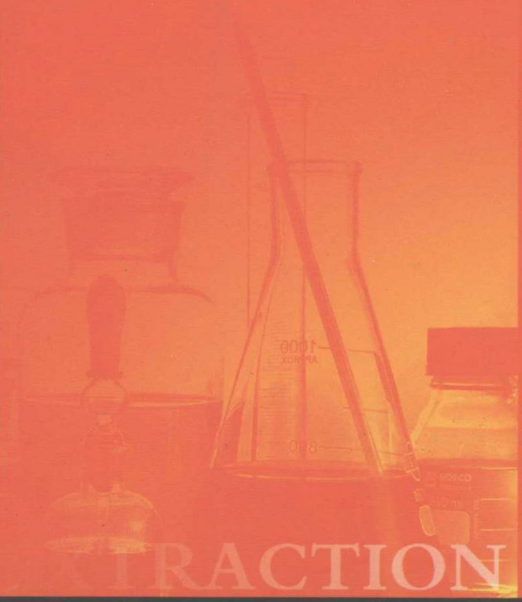

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刘丽娟 著

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中草药中酚苷类物质的研究

STUDIES ON THE PHENOLIC GLYCOSIDES FROM CHINESE MEDICINAL PLANTS

刘丽娟 著

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Introduction

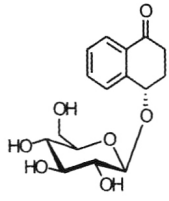
Phenols, widespread in nature, probably constitute the largest group of plant secondary metabolites and are important constituents of many medicinal plants. They range from simple structures with one aromatic ring to highly complex polymeric substances and mostly occur in combination with sugars. The phenolic glycosides in plants have been known for more than a century. Since Piria isolated salicin from *Populus* and *Spiraea* species in 1845,[1] several hundreds of naturally occurring glycosides have been identified and their distribution is widespread.

The phenolic glycosides are divided into eight classes of pharmaceutical interests by the pattern of their aglycones. Namely: 1) simple phenolic glycosides, 2) tannin glycosides, 3) coumarin glycosides,4) anthraquinone glycosides, 5) naphthoquinone glycosides, 6) flavone and related flavonoid glycosides, 7) anthocyanidin and anthocyanin glycosides, 8) lignan and lignin glycosides. A vari-

ety of functions resulting from the diversity of their glycones and aglycones have been ascribed to phenolic glycosides in plants. In the food industry they are utilized as colouring agents, flavourings, aromatizers and antioxidants. For medicinal purposes, they have been developed into anti-inflammatory, anti-cancer, antioxidant and anti-platelet agents. The best-known example of phenolic glycosides used as anti-cancer drugs is Podophyllotoxin and related lignan glycosides from Podophyllum. The discovery of their cytotoxic properties has made Podophyllum a commercially important medicinal plant.

Current estimates of the number of species of flowering plants range between 200 000 and 250 000 in some 300 families and 10 500 genera in the world. [2] Despite a rapidly expanding literature on phytochemistry, only a small percentage of the total species has been examined chemically, and there is still a large field for further research. In China, the employment of medicinal plants in healthcare exceeds that of Western drugs and of acupuncture and there is now an increasing use of Chinese medicinal plants outside China and Asia. [3] However, much is known about the pharmacological and clinical evidence, very much less about the chemical research on some medicinal plants, especially that being used as folk medicine. In the course of

the investigation on the glycosides of Chinese medicinal plants in our department, several other types of new glycosides have been isolated, such as triterpenoid saponins and diterpenoid glycoside. [4,5] As a part of our continuing study, my work therefore extended to the isolation and structural elucidation of phenolic glycosides from four species of Chinese medicinal plants, which have been widely used in clinics but lack of chemical work, including the fruits of *Juglans mandshurica*, the stems of *Tinospora sinensis*, the leaves of *Mallotus furetianus* and the seeds of *Cucurbita moschata*.



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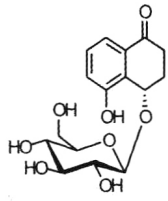

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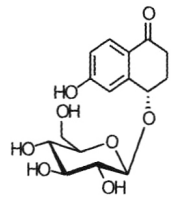

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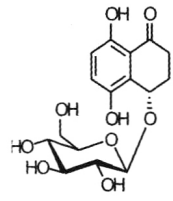

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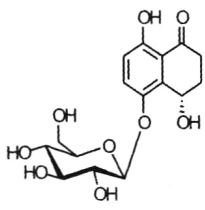

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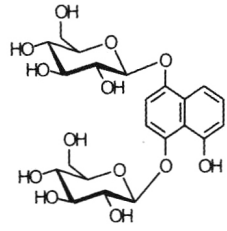

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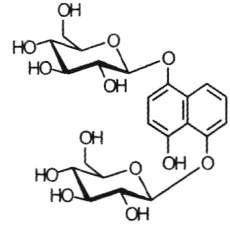

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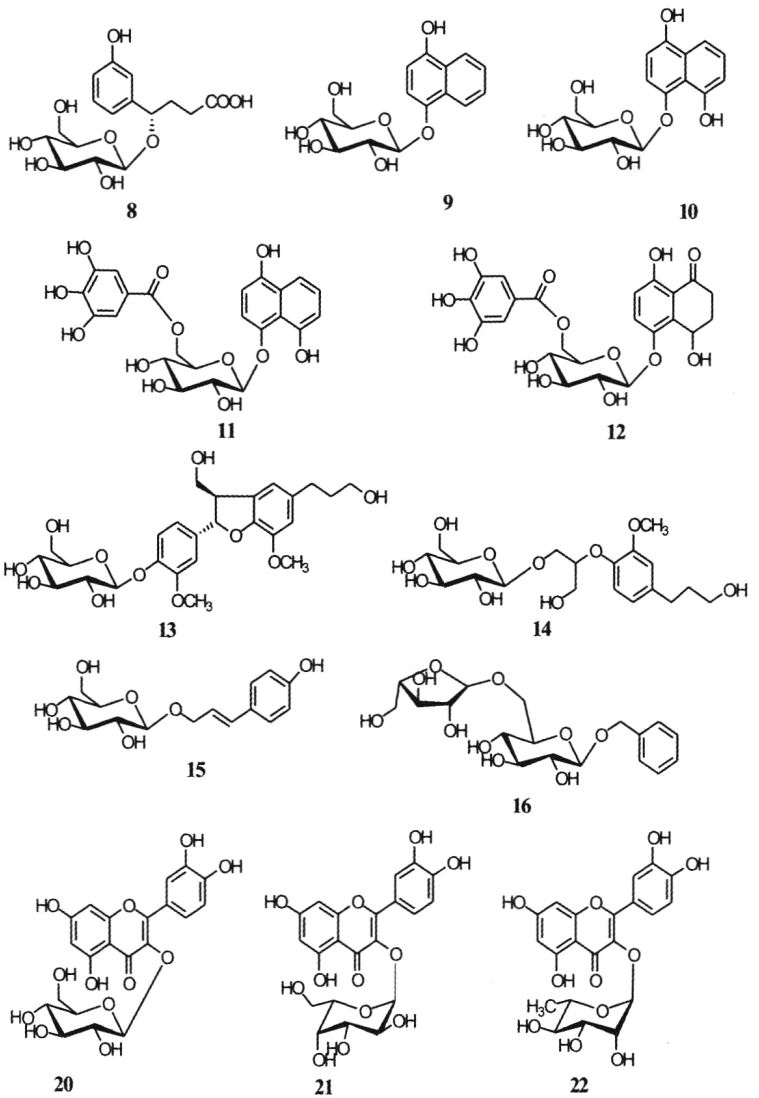


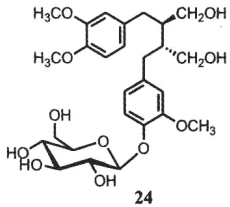
Figure 1 Phenolic Glycosides Isolated from the Fruits of *Juglans mandshurica*

Juglans mandshurica Maxim. (Juglandaceae) is widespread in the urban and rural areas of Heilongjiang Province of China, blessed with abundant medicinal plants. Its fresh rejuvenated fruits, commonly called "Qing Long Yi" (青龙衣) were firstly adopted by *Kai Bao Ben Cao* (开宝本草).[6] It has long been used as a folk medicine for treatment of cancer and dermatosis and as an anodyne to relieve aches.[7] As the phenolic compounds are hard to isolate from aqueous extracts by common means of isolation in the past, there are almost no reports about the chemical constituents of "Qing Long Yi" until now. Nevertheless, the reports concerning pharmacological and clinical evidence are in large quantities and are still increasing in China. Much attention has been drawn to the effective constituents of "Qing Long Yi" with the development of the isolation techniques, so that the quality control of the agents could be available on the basis of the chemical components. Furthermore, *J. mandshurica* is a representative plant growing in northeast of China, especially in Heilongjiang Province. How to explore this plant resource rationally and how to make it feasible to control the quality of its agents become two paramount important topics for the domestic chemical researchers. Thus, efforts have been invested into the study on the chemical constituents of "Qing

Long Yi", resulting in the isolation of 19 phenolic glycosides including 8 novel compounds, juglanosides A—H (1—8) (Figure 1). Their structures were elucidated on the basis of spectroscopic analysis and chemical evidence. The isolated compounds are classified as α-tetralonyl glucosides (1—5, 12)[8], naphthalenyl glucosides (6,7,9—11)[9], flavonoid glycosides (20—22) and other aromatic glycosides. All these compounds were examined for their cytotoxic activities against three tumor cell lines (Human myeloid leukemia HL-60 cells, Human stomach KATO-Ⅲ adenocarcinoma and human lung A_{549} adenocarcinoma) and the results showed that the naphthalenyl glucosides may be related to the antitumor property of "Qing Long Yi".[10]

Tinospora sinensis Merr. (Menispermaceae) and *Mallotus furetianus* (Bail.) Muell-Arg. (Euphorbiaceae) are both tropical plants indigenous to Hainan Island of China, which is famous for being abundant of medicinal plants. The stems of *T. sinensis*, commonly called "Shen Jin Teng"(伸筋藤) in Chinese, were adopted by *Dictionary of Chinese Material Medica* and described as therapeutics of rheumatism, bruises with pain and lumbar muscle strain.[11] Also, pharmacological studies on this plant have demonstrated anti-inflammatory[12], immunomodulatory[13],

and antidiabetic[14] activities and it has been developed into agents combining with other medicinal plants for the treatment of disease relating to rheumatism. Unfortunately, the chemical constituents of "Shen Jin Teng" has not been known clearly until now and so it is impossible to value or control the quality of the agents widely used in clinics. The study on the stems of *T. sinensis* resulted in the isolation of 10 phenolic glycosides including 2 novel compounds (tinosposide A and B, 24 and 25)[15] (Figure 2). Their structures were elucidated on the basis of spectroscopic analysis and chemical evidence. They are classified as lignan glycosides (24—30) and phenylpropenoid glycosides (31—33).



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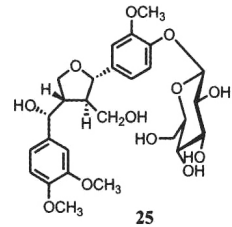

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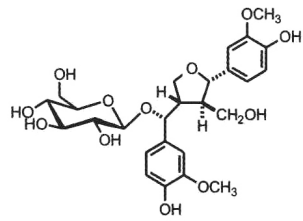

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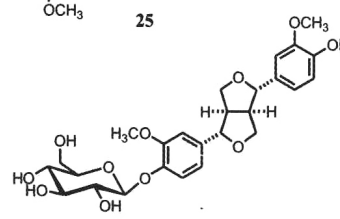

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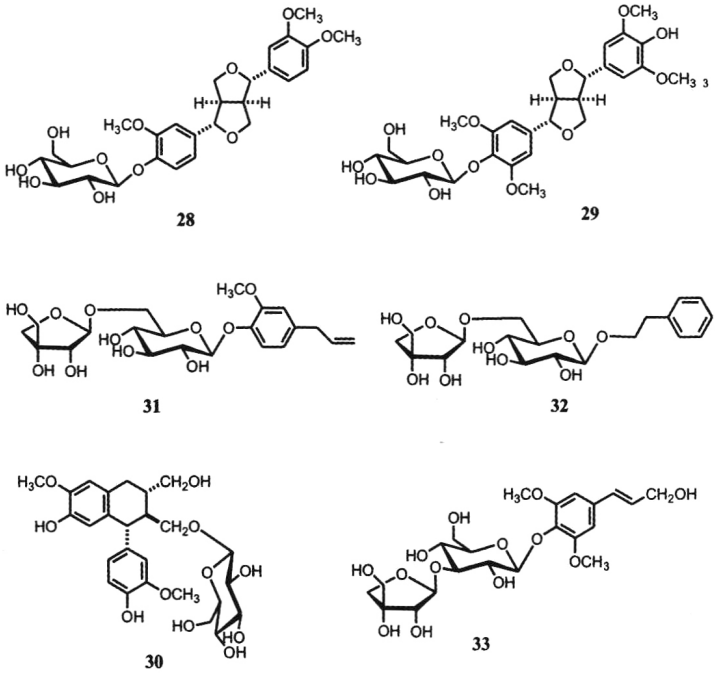

Figure 2 Phenolic Glycosides Isolated from the Stems of *Tinospora sinensis*

The leaves of *Mallotus furetianus*, commonly called "Shan Ku Cha"(山苦茶), adopted by *Flora of Hainan*,[16] have been used as a popular aromatic beverage for indigestion. For medicinal purposes, it is taken to clear "heat" and "toxins" in the body and to quench thirst, and is also used as a folk medicine for the treatment of cholecystitis disease.[17] Reports about its chemical work have

not been found until that was done by our department. 4 phenolic glycosides were isolated including 2 new compounds(mallophenols A and B, 34 and 35)[18] (Figure 3). Their structures were elucidated on the basis of spectroscopic analysis and chemical evidence. They were galloylglucosides(34, 35) and lignan glycosides(37, 38).

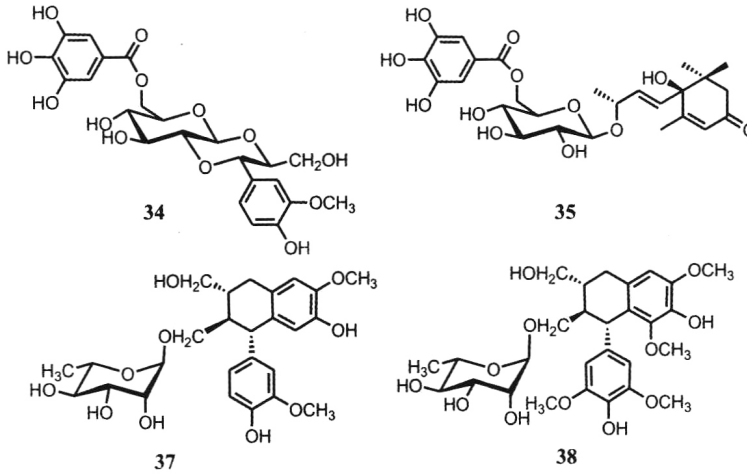

Figure 3 Phenolic Glycosides Isolated from the Leaves of *Mallotus furetianus*

The seeds of *Cucurbita moschata* (Cucurbitaceae), collected in Heilongjiang Province of China are also important traditional Chinese medicine adopted by *Dictionary of Chinese Material Medica.* [19] They are conventionally used for the treatment of cestodiasis, ascariasis, and schistosomiasis[20] and have many reports on the related pharmaco-

logical and clinical evidence. Most of the chemical studies on the pumpkin seeds were carried out on lipids in the pumpkin seed oil[21-23] and no report has been published concerning the water-soluble constituents. Futhermore, pharmacological studies on the seeds have demonstrated hepatoprotective[24] and antitumor activities[25] and have clinical reports about treatment of prostatitis and benign prostatic hyperplasia[26]. This prompt us to investigate the seeds of *Cucurbita moschata*, resulting in the isolation of 5 new phenolic glycosides (cucurbitosides A—E, 42—46)[27] (Figure 4). Their structures were elucidated on the basis of spectroscopic analysis and chemical evidence.

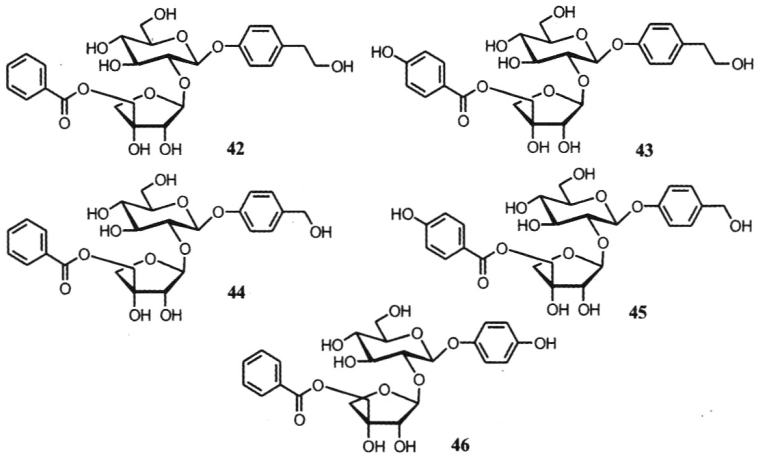

Figure 4 Phenolic Glycosides Isolated from the Seeds of *Cucurbita moschata*

All these four plants are being used as folk medicine in China and there is a considerable and growing literature of clinical and other experimental evidence, however, very much less concerning chemical constituents on these plants. Since Chinese medicinal plants has a strikingly persistent tradition, surviving cultural and dynastic revolutions and there is now an increasing use outside China as mentioned before, it is therefore of paramount importance that the constituents of these plants should be well known. So that the situation regarding the quality of the plants and agents used by manufacturers or sold directly to the public can be well established and these plant resources can be well explored and utilized.