



# Chemical constituents of *Toona microcarpa* (C. DC.) Harms in Engl. (Meliaceae)

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## 1. Subject and source

The use of leaves, seed, and root bark of *Toona microcarpa* (C. DC.) Harms in Engl. in Chinese folk medicine has a long history (Wu, 1988). *T. microcarpa* is a tall tree distributed in India, Myanmar, Sikkim, Indochina and southern China. The stem and bark of *T. microcarpa* were collected in Mar 2006 from Xishuanbannan, Yunnan Province of China. Voucher specimen (No. KUN 0620073) is deposited in Kunming Institute of Botany, Kunming, PR China.

## 2. Previous work

The genus *Toona* comprises five species: *Toona ciliata* Roem. (also known as *Toona sureni* (Bl.) Merr.; *Cedrela toona* Roxb.; syn. *Toona australis*), *Toona sinensis* Roem. (also known as *Cedrela sinensis* A. Juss.), *T. microcarpa* Harms in Engl., *Toona febrifuga* Roem., and *T. calantas* Merr. & Rolfe, the first four can be found at low altitudes in China (Peng and Jennifer, 2008; Wu and Chen, 2004). Previous phytochemical investigations on the genus *Toona* were confined to two species, *T. ciliata* and *T. sinensis*. The investigations of *T. ciliata* have shown that it contains limonoids especially B-seco type (Aghoramurthy et al., 1962; Agostinho et al., 1994; Banerji and Mitra, 1975; Chatterjee et al., 1971; Chen et al., 2009; Hodges et al., 1963; Kraus et al., 1978, 1982; Kraus and Kypke, 1979; Kraus and Grimminger, 1980, 1981; Liao et al., 2007; Mulholland and Taylor, 1992; Neto et al., 1995, 1998), steroids (Chowdhury et al., 2002, 2003), and phenylpropanoids (Bhatia et al., 1969; Chowdhury, 2004; Singh and Plant, 1995). Investigations of *T. sinensis* have found B, D-seco obacunone-type limonoids (Luo et al., 2000; Mitsui et al., 2004) and D-seco gedunin-type limonoids (Mitsui et al., 2006), triterpenoids (Mitsui et al., 2005, 2007), and flavonoids (Hsieh et al., 2006; Wang et al., 2006), which are quite different from those reported from *T. ciliata*.

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However, there are no reports of the phytochemistry of *T. microcarpa*. Therefore an investigation was undertaken to see whether the limonoids of the stem and bark of *T. microcarpa* compared with those in *Toona sinsensis* and *T. ciliate*.

### 3. Present study

Powdered air-dried stem and bark of *T. microcarpa* (9.5 kg) were extracted with 95% EtOH for three times. The extracts were combined and concentrated, followed by suspension in water. The water layer was further extracted with petroleum ether, EtOAc, and *n*-BuOH respectively. The EtOAc extract (180 g) was then subjected to silica gel column eluted with PE/acetone (from 10:1 to 6:4), then eluted with CHCl<sub>3</sub>/MeOH (from 10:1 to 8:2) giving five fractions (F1–F5). The fraction F2 (11.8 g) was subjected to an MCI gel column (MeOH/H<sub>2</sub>O 5:5 to 10:0), and further purified by Sephadex LH-20, silica gel column, and semipreparative HPLC to give (+)-catechin **1** (12 mg) (Nonaka et al., 1983), (6R,7S,8S)-7a-[(β-D-glucopyranosyl)oxy]lyoniresinol (**2**) (7 mg) (Yang et al., 2005), (6R,7R,8R)-7a-[(β-D-glucopyranosyl)oxy]lyoniresinol (**3**) (9 mg) (Yang et al., 2005), and 20-hydroxyecdysone (**4**) (3 mg) (Miller et al., 1985). The spectral data of above known compounds (**1–4**) (Fig. 1) were in agreement with the literature data.

### 4. Chemotaxonomic significance

The position of the genus *Toona* in the family Meliaceae underwent several changes. *Toona* was originally a section of *Cedrela* as described by Endlicher (1840) and was later raised to generic rank (Roemer, 1846). Harms (1940) placed the genus in the tribe Cedrelea under the subfamily Cedreloideae, while Pennington and Styles (1975) included it in the subfamily Swietenioideae. However, the phytochemistry investigations on the *T. ciliate* did not support the affiliation of *Toona* with the Cedreloideae subfamily, but to the subfamily Swietenioideae (da Silva et al., 1984; da Silva and Gottlieb, 1987; Agostinho et al., 1994; Neto et al., 1995, 1998). Furthermore, da Silva et al. (1999) suggested treating the genus as a separate subfamily Toonoideae, which was echoed by Liao et al. (2007). Chowdhury (2004), however, proposed including the genus *Toona* in the Toonoideae or Cedreloideae subfamily along with *Cedrela*.

However, the above chemotaxonomy discussions were based mainly on the phytochemistry studies of the limonoid chemistry of *T. ciliate*. The chemistry of *T. sinensis* was not included in the discussion and the chemistry of *T. sinensis* (Hsieh et al., 2006; Luo et al., 2000; Mitsui et al., 2004, 2005, 2006, 2007; Wang et al., 2006) differs from that of *T. ciliate*.

Besides, Mulholland and Taylor (1992) confirmed that *T. australis* (F. Muell.) Harms is conspecific with *T. ciliate* as they detected the limonoid cedrelone which is present in the timbers of both species. Therefore, we investigated the stem and bark of *T. microcarpa* in attempt to clarify the taxonomic position of the genus whether in Cedreloideae or Swietenioideae subfamily and the relationship of the species to *T. ciliate* and *T. sinensis*.

It was hoped that further limonoids would be isolated from *T. microcarpa*. A flavanone, two lignans, and a steroid were obtained but no limonoid was detected. This represents the first report on the chemical constitution of *T. microcarpa*, in which (+)-catechin (**1**) has also been found in *T. ciliate* (Bhatia et al., 1969) and *T. sinensis* (Hsieh et al., 2006), confirming placement of

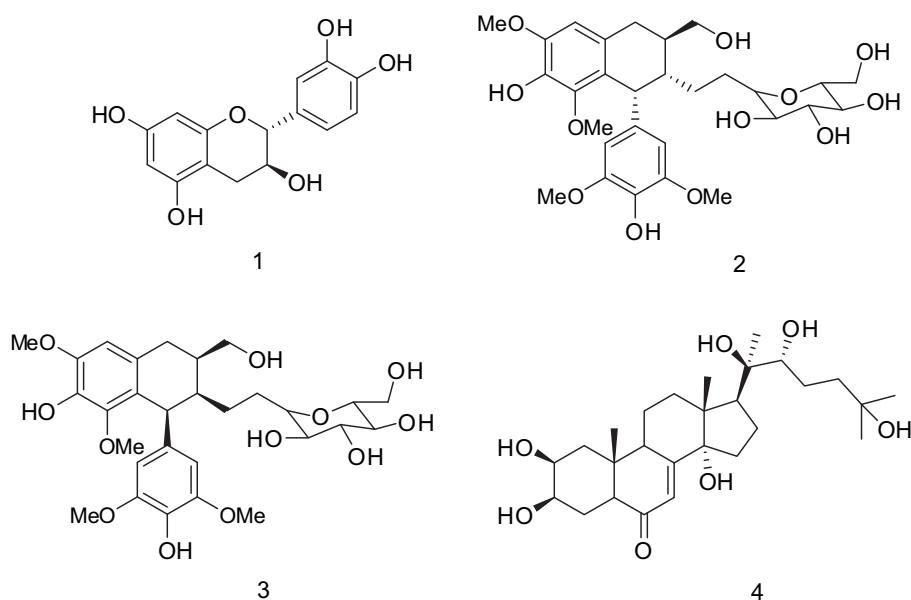


Fig. 1. Structures of compounds isolated from *T. microcarpa*.

*T. microcarpa* in the genus. Neither (6R,7S,8S)-7a-[( $\beta$ -D-glucopyranosyl)oxy]lyoniresinol (**2**) nor (6R,7R,8R)-7a-[( $\beta$ -D-glucopyranosyl)oxy]lyoniresinol (**3**) has been isolated previously from the genus. This is also the first time that lignans was isolated in the genus. Although 20-hydroxyecdysone (**4**) has not been obtained from the genus before, *T. ciliate* is known to produce steroids, which might imply that *T. microcarpa* is more close to *T. ciliate* than *T. microcarpa* is to *T. sinensis*. It is also noteworthy that lignans and steroids were mainly found in the Cedreloideae subfamily (Zhou and Duan, 2005), which confirmed the suggestion of including the genus *Toona* in the Cedreloideae or Toonoideae subfamily (Chowdhury, 2004).

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## Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.bse.2009.12.039](https://doi.org/10.1016/j.bse.2009.12.039).

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