Chemical constituents from *Caragana tangutica*

Xiao-Feng Niu, Yong-Mei Li, Hua Hu, Xia Liu*, Lin Qi

School of Pharmacy, Health Science Center, Xi’an Jiaotong University, No. 76, Yanta Weststreet, Xi’an, Shaanxi Province 710061, PR China

**Abstract**

Phytochemical investigation of *Caragana tangutica* Maxim. resulted in the isolation of ten flavonoids, melilotocarpan A (1), medicarpin (2), maackiain (3), 2-(2,4'-dihydroxyphenyl)-3-methyl-6-methoxy benzofuran (4), cajanin (5), formononetin (6), 7,3',5'-trihydroxy-5-methoxy isoflavone (7), texasin (8), 2',4',4'-trihydroxy chalone (9) and bolusanthin III (10), as well as one aromatic acid, p-ethoxy benzoic acid (11). Compounds 1, 4, 9, 10 and 11 were isolated for the first time from the genus *Caragana*. The chemotaxonomic significance of these compounds was summarized.

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1. Subject and source

The genus *Caragan* (Fabaceae) consists of about 100 species, mainly distributed in the arid and semi-arid areas of Asia and Eastern Europe. There are 62 species grown in China. Members of the genus *Caragana* have been used as traditional Chinese medicine to treat hypertension, breast cancer, wounds and arthritis (Flora Compilation Committee of Chinese Academy of Science, 1993; Jiangsu New Medical College, 1985; Meng et al., 2009). *Caragana tangutica* Maxim., called “Zuomaoxing” in Chinese, is a perennial herb grows in valleys at about 3600 m altitude, and distributes in south Gansu, east Qinghai, northwest Sichuan and Tibet in China (Wu, 1985). The heartwood of *C. tangutica* has been used by local inhabitants as Tibetan medicine for the treatment of trauma and injury, rheumatic pains, irregular menstruation and inflammation in breasts (Northwest Institute of Plateau BiologyChinese Academy of Sciences, 1996). The heartwoods of *C. tangutica* were collected from Changdu county, Tibet of P. R. China in August, 2011, and were identified by Prof. Xiao-Feng Niu, Xi’an Jiaotong University, Xi’an, P. R. China. A voucher specimen (No. 2011-08-05) has been deposited at the Herbarium of the School of Medicine, Xi’an Jiaotong University.

2. Previous work

Species *Caragana* are reported to contain compounds such as flavonoids, stilbenoids, terpenoids, steroids and phenylpropanoids. Among them, flavonoids and stilbenoids are reported as the major components of this genus (Meng et al., 2009; Yang et al., 2008; Zhang et al., 2009). To date, the chemical composition of *C. tangutica* has not been studied.

3. Present study

The air-dried heartwoods of *C. tangutica* (2.0 kg) were powdered and extracted with 90% ethanol (3 × 5 L) under reflux for 2 h each time. The combined extracts were evaporated in vacum to obtain 206 g of syrupy residue, which was then resuspended in water and partitioned successively with EtOAc and n-BuOH. The EtOAc extract (70 g) was subjected to silica gel
column chromatography (1000 g, 200–300 mesh), eluted with a gradient of petroleum ether:acetone (50:1, 20:1, 15:1, 10:1, 5:1, 2:1, 1:1) to afford seven fractions Fr. I–VII. Fr. II (13 g) was separated into three subfractions (Fr. IIA–Fr. IIC) by column chromatography using petroleum ether:ethyl acetate (20:1) as eluent. In which Fr. IIA (3.8 g) was further fractionated on a silica gel column using petroleum ether:ethyl acetate (25:1) to elute to yield compound 1 (280 mg). Fr. IIB (3.0 g) was further fractionated on a silica gel column using petroleum ether:ethyl acetate (10:1) as eluent to afford compounds 2 (135 mg) and 11 (15 mg). Fr. IIC (1.5 g) was subjected on a silica gel column eluting with petroleum ether:ethyl acetate (8:1) to obtain impure 3, which was further purified by recrystallization using ethanol to give pure 3 (85 mg). Fr. III (12 g) was chromatographed on silica gel column and eluted with petroleum ether:acetone (9:1) to give four subfractions Fr. IV–Fr. V. Fr. IV (5 g) was separated by column chromatography and eluted with chloroform:ethyl acetate (9:1) to give one subfraction. Fr. V (2.4 g) was subjected to silica gel column eluting with chloroform:acetone (20:1) to produce compound 4 (13 mg). Fr. VI (1.2 g), which was chromatographed on silica gel column and eluted with chloroform:methanol (50:1).

The compounds were identified as melilotocarpan A (1) (Lotti et al., 2010), medicarpin (2) (Yoon et al., 2004), maackiain (3) (Baruah et al., 1984), 2-(2′,4′-dihydroxyphenyl)-3-methyl-6-methoxy benzofuran (4) (Awale et al., 2008), cajanan (5) (Waffo et al., 2000), formononetin (6) (Chang et al., 1994), 7,3′-dihydroxy-5-methoxy isoflavone (7) (Sun et al., 2010), texasin (8) (Kim et al., 2010), 2′,4,4′-trihydroxy chalone (9) (Zhang et al., 2008), bolusanthin III (10) (Erasto et al., 2004) and p-ethoxy benzoic acid (11) (Tang et al., 2001) respectively by comparison of their spectra data with the reported data in the literature (Fig. 1).

4. Chemotaxonomic significance

To the best of our knowledge, this is the first report on the phytochemical study of Caragana tangutica, a total of 11 compounds were isolated and assigned as flavonoids [pterocarps (1–3), 2-arylbenzofuran (4), isoflavones (5–8), chalcone (9) and isoflavan (10)], as well as an aromatic acid (11). Results showed that flavonoids were the major chemical constituents. The chemical composition of this plant was in a good agreement with previous reports concerning other Caragana species. This is also the first report of the presence of compounds 1, 4, 9, 10 and 11 in Caragana species.

Among the isolates, 5 and 7 have been reported from Caragana jubata (Song et al., 2011; Wang et al., 1986), 2 from Caragana tibetica (Xiang et al., 2005) and Caragana spinifera (Deng et al., 2008), 3 from C. jubata (Song et al., 2011), Caragana sinica (Yuan et al., 2007) and Caragana microphylla (Jin et al., 1992), 8 from C. jubata (Wang et al., 1986) and C. spinifera (Deng et al., 2008), and 6 from several Caragana species (Deng et al., 2008; Huo et al., 2007; Jia and Zhou, 1988; Khan et al., 2010; Zhang et al., 1997). It has been reported that C. jubata was also enriched with pterocarps and isoflavones. The compounds 3 and 5–8, were all previously isolated from C. jubata. It indeed appears that the chemical composition of C. tangutica is very close to that of C. jubata.

Fig. 1. Structures of constituents isolated from Caragana tangutica.
Melilotocarpan A (1) was mainly occurred in family Fabaceae (Cheenpracha et al., 2012; Lotti et al., 2010; Wang and Zhang, 2008; Belofsky et al., 2006; Chan et al., 1998; Ingham, 1976). Bolusanthin (10) was only isolated from the root wood of *Bolusanthus speciosus* (Erasto et al., 2004) and 2-(2′,4′-dihydroxyphenyl)-3-methyl-6-methoxy benzofuran (4) was only isolated from the Brazilian red propolis (Awale et al., 2008). 2′,4,4′-Trihydroxy chalone (9) has been reported as the major components of Radix Glycyrrhiza (Zhou et al., 2011).

In conclusion, the results of this study indicate that *C. tangutica* produces the similar pterocarpans and isoflavones as other *Caragana* species and imply a close systematic relationship among *Caragana* genus. This also suggests that the presence of pterocarpans and isoflavones in the *Caragana* genus could be of taxonomic importance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.bse.2013.09.014.

References
