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Comparative profiling of phenolic compounds from different plant parts of six *Terminalia* species by liquid chromatography–tandem mass spectrometry with chemometric analysis

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ABSTRACT

Terminalia species are extensively used as ethno-medicinal and traditional plants. Phenolic compounds extracted from *Terminalia* species have been reported to possess several biological activities. This study reports comparative profiling of phenolic constituents in different plant parts of six *Terminalia* species namely *T. arjuna*, *T. bellerica*, *T. catappa*, *T. chebula*, *T. elliptica* and *T. paniculata* using ultra-performance liquid chromatography coupled with hybrid triple quadrupole-linear ion trap mass spectrometry (UPLC-QqQ_{LIT}-MS/MS). To achieve this target an UPLC-ESI–MS/MS method was developed and validated for the estimation of 37 phenolic compounds. Calibration curves for the selected analytes provided optimum linear detector response (with $R^2 \geq 0.9972$) over the concentration range of 0.5–1000 ng/mL. The results indicated significant variation in the total contents of the 37 compounds in *Terminalia* species and found the most abundant in *T. chebula* fruit. Principal component analysis (PCA) was applied to compare and evaluate the quality of different plant parts of six *Terminalia* species based on the contents of the investigated compounds.

1. Introduction

Terminalia species of Combretaceae family are well known ethno-medicinal and traditional plants (Khatoon et al., 2008). They are deciduous and evergreen trees which attain a height of 6–30 m (Khan et al., 2013; Saha et al., 2012). There are around 250 *Terminalia* species in which at least 50 are used as food worldwide (Ammar et al., 2002). The fruit and bark of *Terminalia* are used as food supplements (Bruce, 2013); bark of *T. bellerica* and *T. elliptica* are used for the preparation of wine and palm sugar (Bruce, 2013); their fruits are used for making preserves and also eaten raw. The nutritional and therapeutic properties are related to the high level of phenolics consisting of flavonoids, phenolic acids, triterpene glycosides, gallotannins, ellagitannins and proanthocyanidins (Anon, 1976; Saraswathi et al., 2012; Padmaa, 2010; Muhammad et al., 2012; Chopra and Ghosh, 1929; Pfundstein et al., 2010). The reported cardio protective and wound healing effects are attributed to the presence of triterpenoids particularly arjunolic acid, arjungenin, arjunetin, and oleanolic acid (Dwivedi, 2007; Zhou et al., 2011a), whereas the anticancer effect is attributed to the presence of betulinic acid. It is worth noting that phenolics present in *Terminalia* species are potent anti-dyslipidaemic, hypocholesterolaemic, anti-acne, anti-helmintic, anti-inflammatory, anti-allergic, anti-bacterial, cytotoxic, anti-asthmatic, anti-fungal and anti-oxidant agents (Cheng et al., 2003; Fyhrquist et al., 2002; Gupta et al., 2001; Shinde et al., 2011; Choudhary, 2008; Ko et al., 2003; Pettit et al., 1996; Dwivedi, 2007; Zhou et al., 2011a,b,c,d). Various *Terminalia* species have been known for their significant ethno-medicinal properties such as *T. arjuna* (Roxb.) Wight and Arn. which is used for the treatment of coughs, dysentery, fractures, contusions, sores, ulcers, hypertension and ischaemic heart diseases; *T. catappa* Linn. for the treatment of dysentery, diarrhea, and bilious fever; *T. chebula* Retz. for the treatment of sores; and *T. elliptica*

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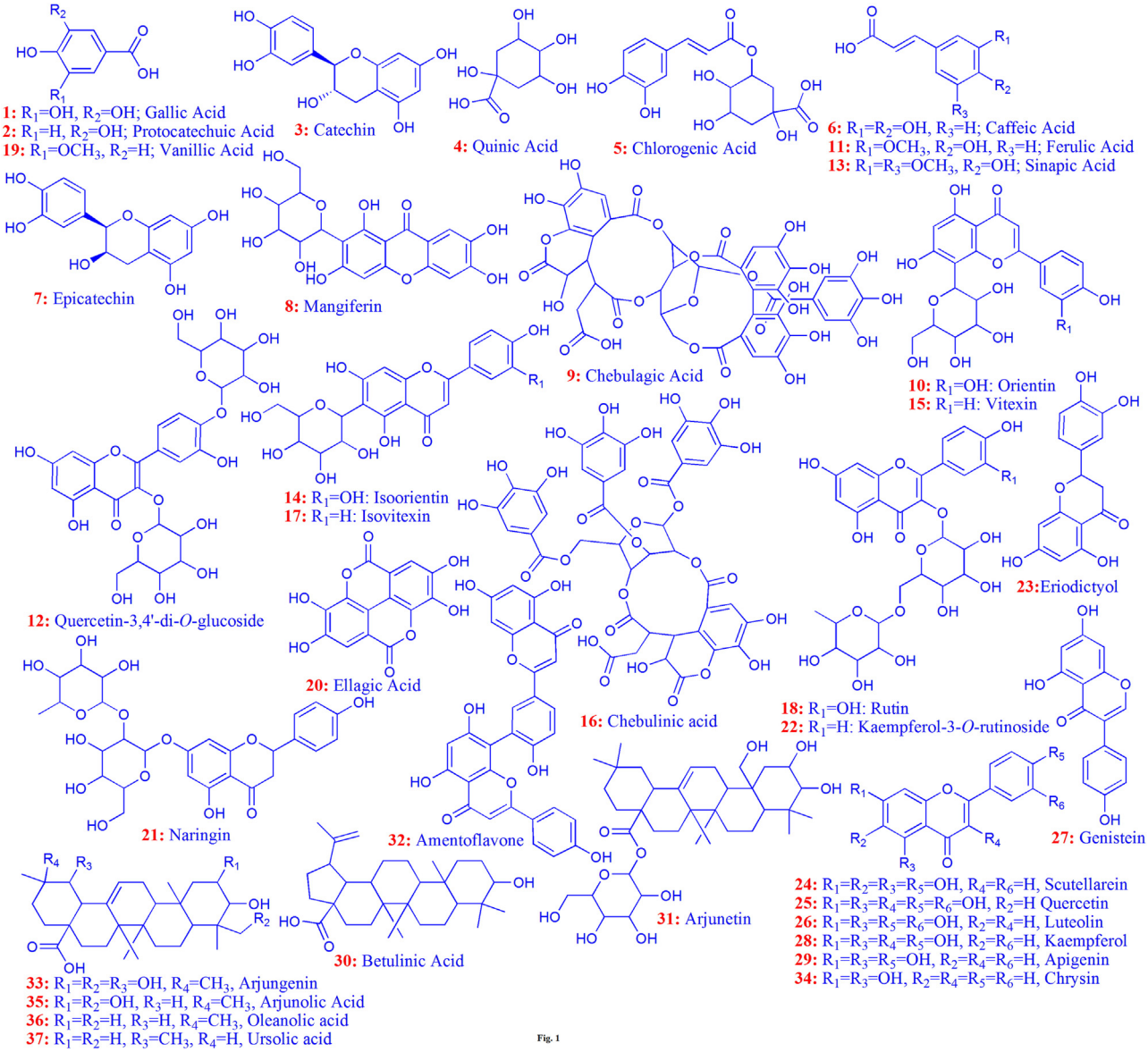

Fig. 1. Chemical structure of bioactive compounds identified in ethanolic extract of *Terminalia* species.

(synonymous *T. tomentosa*) Willd for the treatment of ulcers, fractures, hemorrhages, bronchitis, and diarrhea (Choudhary, 2008; Ko et al., 2003; Chaudhari and Mengi, 2006; Kirtikarand and Basu, 2001; Joshi et al., 2013; Nagappa et al., 2003; Masuda et al., 1999; Ko et al., 2002).

Several analytical methods, such as high-performance thin-layer chromatography (HPTLC), high-performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC–MS), have been used for the determination of phenolic compounds including phenolic acids, flavonoids, triterpene acids, oleane derivatives etc. (Khatoon et al., 2008; Kumar et al., 2010; Kalola and Rajani, 2006; Singh et al., 2002). In the stem-bark of *T. arjuna,* ellagic acid and gallic acid were previously quantified by thin-layer chromatography (TLC) and arjunic acid, arjunolic acid, arjungenin, arjunetin, arjunglucoside I were quantified by HPTLC and TLC desitometry (Khatoon et al., 2008; Kumar et al., 2010; Kalola and Rajani, 2006; Singh et al., 2002). However, these methods suffer from low sensitivity, low resolution and/or long analysis time with consumption of large amount of solvents. Ultra-performance liquid chromatography/triple quadrupole linear ion trap mass spectrometer (UPLC/QqQ$_{LIT}$-MS) enables rapid detection of the targeted analytes at very low concentration levels due to its selectivity and superior sensitivity with low consumption of solvents (Singh et al., 2015; Grace et al., 2007; Wei et al., 2014; Liu et al., 2014; Qiana et al., 2015).

The aim of this study was the comprehensive identification, quantification and discrimination in terms of distribution of phenolic compounds in different plants parts (bark, fruit, leaf, stem, and root) of six *Terminalia* species, namely, *T. arjuna*, *T. bellerica*, *T. catappa*, *T. chebula*, *T. elliptica* and *T. paniculata.* by UPLC-ESI–MS/MS with chemometric analysis.

2. Experimental

2.1. Plant materials

Six *Terminalia* species were collected from Jawaharlal Nehru Tropical Botanic Garden and Research Institute campus (JNTBGRI; N:8°45′, E:77°10′, Altitude: 70–160 m), Kerala, south India in the month of February 2014. Voucher herbarium specimen numbers of