Chemical constituents from *Elegia tectorum* and their chemophenetics importance

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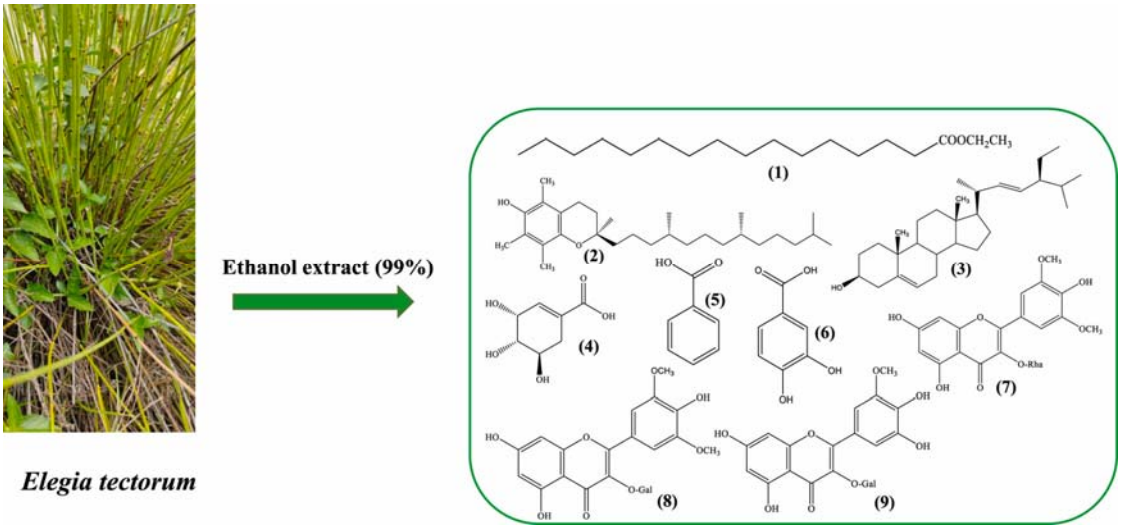
Highlights

- Nine compounds were isolated from *Elegia tectorum*.
- Isolation of fatty acid, chromane derivative, phytosterol, and phenolic derivatives.
- Syringetin and laricitrin galactosides were found.
- Syringetin-3-O-rhamnoside is isolated from *E. tectorum* for the first time.
- Chemophenetics significance among the *Elegia* species was discussed.

Abstract

The phytochemical analysis of *Elegia tectorum* (L.f.) Moline and H.P.Linder led to the isolation of nine chemical constituents, categorized into one fatty acid, one phytosterol, one chromane derivative, three phenolic derivatives, and three flavonoid glycosides. The structure elucidation of the isolated compounds was achieved on the basis of NMR spectroscopy. The presence of flavonol glycosides (syringetin and laricitrin derivatives) in the investigated *Elegia* species is in line with previous findings on the genus *Elegia*. The chemical composition of *E. tectorum* was substantially supplemented. Importantly, the chemophenetics importance of isolated compounds has been discussed.

Graphical abstract



Keywords: *Elegia tectorum;* Restionaceae; Flavonoid glycosides; Phenolic acids; Chemophenetics

1. Subject and source

The Restionaceae family comprises over 500 species and 60 genera, distributed in the southern hemisphere with most of its populations occurring in Africa (ca. 360 species) and in Australia (around 150 species) (Linder et al., 1998; Dorrat-Haaksma and Linder, 2012). The genus *Elegia* L. is the second largest genus of this family and consists of about 52 species, which are distributed to the Western and Eastern Cape Province of South Africa (Linder et al., 1998; Linder and Hardy, 2010; Dorrat-Haaksma and Linder, 2012; Linder, 2018). Among them, *Elegia tectorum* (L.f.) Moline and H.P.Linder could mainly occur in coastal areas in the western and eastern Cape, in the northern mountains of the protected area "Cape Floristic Region", as well as in the west coast and southwestern mountains of South Africa. It is also widespread from the "Clanwilliam" to the "Port Elizabeth" areas (Linder et al., 1998; Dorrat-Haaksma and Linder, 2012; Linder, 2018). This species, along with *Elegia equisetacea* Mast., is widely used for thatching and as materials for brooms (Aston Philander, 2011; Dorrat-Haaksma and Linder, 2012).

In the present study, the stems of *E. tectorum* were collected from Manie van der Schijff Botanical Gardens at the University of Pretoria (25°45′10.4″S 28°13′41.6″E), in March 2016 and verified by the university's herbarium. A voucher specimen (number: 122257) was deposited at the University of Pretoria's herbarium.

2. Previous work

A detailed review of the traditional uses, phytochemistry, and pharmacological activities of *Elegia* species has previously been conducted by our groups (Lymperis et al., 2022). Previous phytochemical studies on *E. tectorum* reported the presence of syringetin, laricitrin-3-galactoside, syringetin-3-galactoside, procyanidin, and prodelphinidin (Harborne, 1979; Harborne et al., 1985). However, there is no report on the extensive investigation of the chemical constituents of this species, up to date. Thus, the present study focuses on the

phytochemical investigation of *E. tectorum* and describes its chemophenetics importance. Furthermore, their anti-elastase potential has been studied based on previous results about this activity of the *E. tectorum* extract (Lymperis et al., 2022).

3. Present study

The grounded freeze-dried stems of *E. tectorum* (307.90 g) were extracted with ethanol (99%) and dried using a rotary evaporator. Part of the ethanol extract (3.23 g) was pre-fractionated by VLC (Vacuum Liquid Chromatography, 8.0 × 9.5 cm) over silica gel, using eluent mixtures of increasing polarity (DCM:MeOH:H_2O 100:0:0–0:50:50) to yield 10 fractions (A-J). Fraction C (62.6 mg; eluted with DCM 100%) was submitted in prep-TLC over silica gel with CyHex:DCM 30:70 to afford compounds **1** (Rf: 0.72; 1.0 mg) and **2** (Rf: 0.55; 1.2 mg). Fraction D (249.6 mg; eluted with DCM:MeOH 90:10) was submitted to CC (Column Chromatography, 9.5 × 2.5 cm) over silica gel (CyHex:DCM:MeOH 100:0:0–0:0:100) and yielded compound **3** (2.5 mg). Fraction E (794.1 mg; eluted with DCM:MeOH 80:20) was subjected to CC (19.5 × 3.5 cm) over silica gel (DCM:MeOH:H_2O 90:10:1.0) and afforded compounds **5** (1.0 mg) and **7** (2.0 mg). Fraction F (524.7 mg; eluted with DCM:MeOH 70:30) was subjected to CC (19.5 × 2.5 cm) on Sephadex LH-20 with isocratic elution (MeOH:H_2O 70:30), giving compounds **4** (25.3 mg), **6** (1.0 mg), **8** (1.3 mg) and **9** (2.0 mg).

Thereafter, the potential anti-elastase activity of the compounds was assessed following the method of Nel et al. (2022).

4. Chemophenetics importance

The present phytochemical study revealed the isolation of nine chemical constituents from the ethanol stem extract (99%) of wild *E. tectorum*, one fatty acid ester, ethyl palmitate (**1**) (Nazeam et al., 2018); one chromane derivative, α-tocopherol (**2**) (dos Santos et al., 2014); one phytosterol, stigmasterol (**3**) (Singh et al., 2015); three phenolic derivatives, namely shikimic acid (**4**) (Venditti et al., 2017), benzoic acid (**5**) (Chen et al., 2008), protocatechuic acid (**6**) (Masuoka et al., 2007) and three flavonoid glycosides, syringetin-3-O-rhamnoside (**7**) (Braca et al., 2001), syringetin-3-O-galactoside (**8**) (Masuoka et al., 2007), laricitrin-3-O-galactoside (**9**) (Braca et al., 2001) (Fig. 1). Compounds were identified using GC-MS technique (for compounds **1** and **2**), NMR spectroscopy (for compounds **3**–**9**) and comparisons with the literature data. Among them, compounds **1**–**6** are isolated for the first time in the genus *Elegia*. It is worth mentioning that compound **1** might be an artifact since ethanol was used as an extraction solvent which could form ethyl esters from compounds with carboxylic acid (Venditti, 2018). Further study with the use of a different extractive solvent should be carried out in order to investigate the presence of such esters.

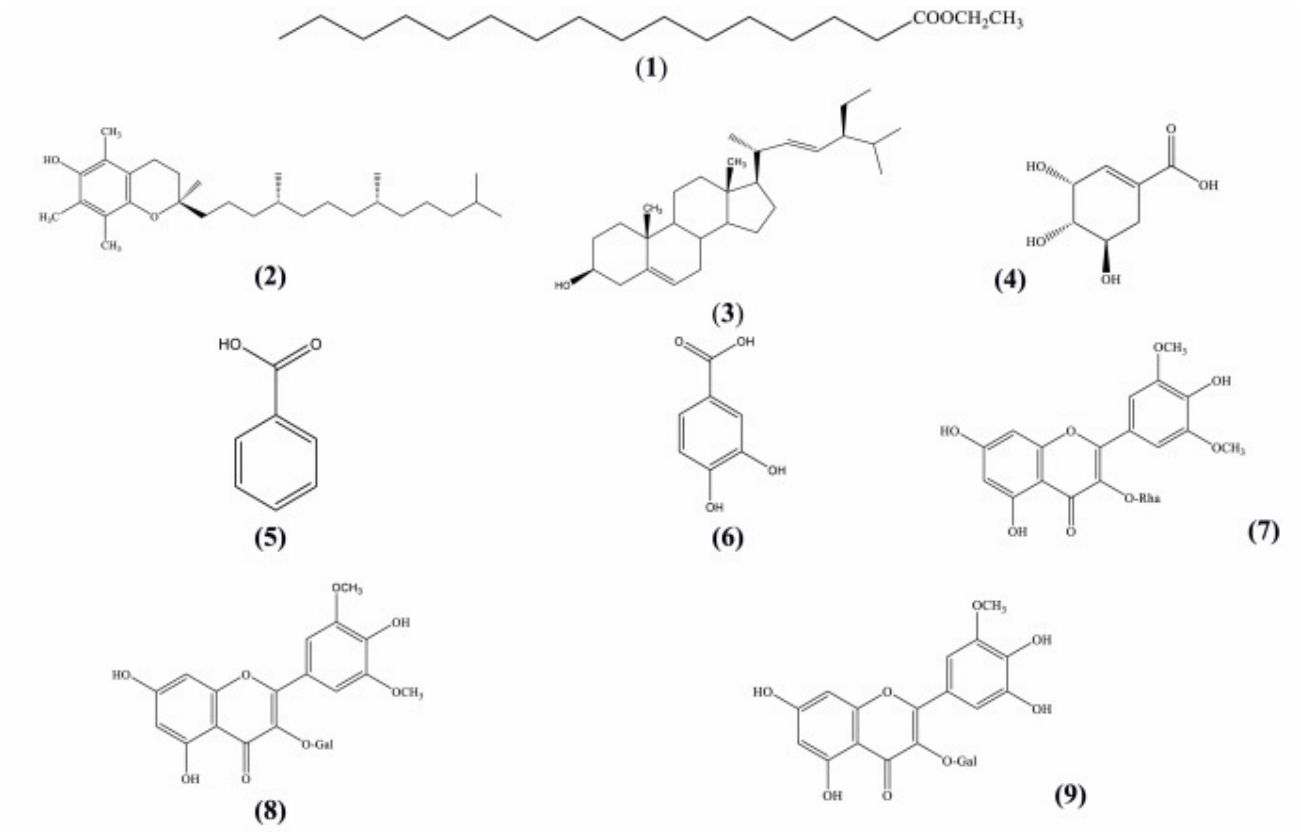


Fig. 1. Structures of compounds **1**–**9** isolated from *E. tectorum*.

Flavonoids are the major constituents of the Restionaceae family with African species being rich in 3-hydroxyflavones (flavonols) and flavones (aglycons or/and with their glycosides) (Lymperis et al., 2022). The genus *Elegia* is characterised by the presence of flavonol glycosides: myricetin, laricitrin, and syringetin, while glycosides of flavones are not present (Lymperis et al., 2022). This distinguished them from the rest of the African genera which could contain quercetin and glycosides of luteolin, apigenin, chrysoeriol, cyanidin, orientin, iso-orientin, and lucenin (Harborne, 1979; Linder et al., 1998). Over the years, many *Chondropetalum* species were eventually reclassified to the genus *Elegia* (Harborne et al., 1985). In a previous study, 11 species of the genus *Chondropetalum* were investigated for their chemical profile, and most of the examined *Chondropetalum* species were eventually reclassified to the genus *Elegia*, while the rest belong to the genus *Askidiosperma* (Harborne et al., 1985). The species were also divided into two groups; the first group included most species re-classified to the genus *Elegia* and contained glycosides of myricetin, laricitrin, and syringetin and the second group consisted of mainly *Askidiosperma* species, which contain quercetin, kaempferol, gossypetin, 7-O-methyl-ether of gossypetin and herbacetin 4′-methyl ether. Previous studies reported the flavonols glycosides in 13 *Elegia* species, namely *E. capensis* (Burm. F.) Schelpe, *E. cuspidata* Mast., *E. deustum* (Rottb.) Kunth, *E. filacea* Mast., *E. galpinii* N. E. Br., *E. hookeriana* (Mast.) Moline and H.P.Linder, *E. microcarpa* (Kunth.) Moline and H.P.Linder, *E. mucronata* (Nees) Kunth, *E. nuda* (Rottb.) Kunth, *E. persistens* Mast., *E. recta* (Mast.) Moline and H.P.Linder, *E. spathacea* Mast., and *E. tectorum* (Lymperis et al., 2022). Interestingly, myricetin glycosides have not been found in all *Elegia* species, including *E. tectorum*. Our results are in line with previous findings since the isolated flavonols (compounds **7**–**9**), which are glycosides of laricitrin and syringetin, confirm their presence in

the genus *Elegia* and in the specific species they could be used as potential characteristic markers. Compound **7** was found only in *E. deustum*, while this is the first report on its presence in *E. tectorum*. Compounds **8** and **9** have been previously mentioned in various *Elegia* species, including *E. tectorum* (Lymperis et al., 2022).

Although procyanidin and prodelphinidin could be found in some *Elegia* species (*E. capensis*, *E. cuspidata*, *E. deustum*, *E. filacea*, *E. galpinii*, *E. microcarpa*, *E. mucronata*, *E. nuda*, *E. persistens*, *E. recta*, and *E. tectorum*) (Lymperis et al., 2022), this study did not reveal their presence in *E. tectorum*. This might be attributed to the different geographical origins or extraction methods.

Lastly, the present work also investigated the anti-elastase potential of the nine isolated compounds, aiming to explore the responsible compounds of the *E. tectorum* extract based on a previous study (Lymperis et al., 2022). However, none of them displayed significant activity at 500 μg/mL, while ursolic acid (positive control) had an IC_{50} value of 22.30 ± 2.79 μg/mL. Thus, the anti-elastase activity of *E. tectorum* might be due to a synergy of the compounds or compounds not isolated during this study.

In summary, the present phytochemical study revealed the isolation of nine chemical constituents from the ethanol stem extract (99%) of wild *E. tectorum*. In addition, no significant anti-elastase activity was observed by the isolated compounds. This work not only extends the phytochemical knowledge of *E. tectorum*, but also sheds light on its further phytochemical and chemophenetics investigation.

CRediT authorship contribution statement

Panagiotis Lymperis: Writing – original draft, Investigation. **Ekaterina-Michaela Tomou:** Writing – original draft, Investigation. **Bianca D. Payne:** Writing – review & editing, Investigation. **Marizé Cuyler:** Writing – review & editing, Investigation. **Namrita Lall:** Writing – review & editing, Conceptualization. **Helen Skaltsa:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data that has been used is confidential.

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