# Activity of SDH, QDH, and PAL in species, accumulating different types of tannins

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# Abstract

The biosynthesis of different classes of tannins in plants is a complex process that remains insufficiently studied. This study aimed to evaluate the activity of shikimate dehydrogenase (SDH), quinate dehydrogenase (QDH), and phenylalanine ammonia-lyase (PAL), and their influence on the accumulation of proanthocyanidins (PA) and/or hydrolyzable tannins (HT) in medicinal plants. The leaves of *Hippophae rhamnoides* and *Cornus sericea* (accumulating HT), *Astilbe chinensis* (accumulating PA), and *Agrimonia pilosa* and *Agrimonia asiatica* (accumulating both HT and PA) were used in the present study. The highest PA levels were found in *A. chinensis*, while the highest HT content was observed in *H. rhamnoides*. Water-soluble PA predominated in all species. The highest SDH activitiy were detected in the leaves of the HT-rich species *C. sericea* and *H. rhamnoides*, while QDH activity was comparatively low. Activity of PAL was the highest in the leaves of *H. rhamnoides*, and the lowest – in *A. chinensis.* Correlation analysis revealed a positive relationship between SDH activity and HT levels. No significant correlation was found between QDH or PAL activity and tannin content. These findings add valuable information into the enzymatic regulation of tannin biosynthesis in medicinal plants that accumulate different types of tannins.


# Introduction

Tannins are a chemically diverse group of phenolic compounds that play an important role in plant adaptation, stress defense and protection from insects and herbivores. They are commonly classified into hydrolyzable (HT), condensed tannins (proanthocyanidins, PA) and phlorotannins. Their biosynthesis is a complex process closely related to shikimate pathway, one of the key enzymes of which is bifunctional dehydroquinate dehydratase/shikimate dehydrogenase (DQD/SDH) – a branch point for HT synthesis through gallate formation (Ossipov et al. 2003; Singh and Christendat 2006). Quinate dehydrogenase (QDH) is the SDH paralogue, converting 3-dehydroquinate (3-DHQ) to quinate. The final product of the shikimate pathway, chorismate, is converted into L-phenylalanine – a precursor of phenylpropanoids, flavonoids, and PA, via phenylalanine ammonia-lyase (PAL) (Fig. 1). The biosynthesis of HT and PA in plants diverges at critical branch-points in metabolism. A key branch-point is 3-dehydroshikimate (3-DHS), the substrate of SDH. SDH can channel 3-DHS in two directions: (1) reduction to shikimate, leading eventually to chorismate and aromatic amino acids, or (2) oxidation to form gallic acid, the precursor of HT (Ossipov et al. 2003; Guo J 2014; Bontpart et al. 2016) (Fig. 1).

Most existing researches focus on a single plant species, often in response to environmental or stress-related factors (Díaz et al. 2001; Habashi et al. 2019). In our previous study, we conducted a comparative analysis of enzyme activities in three *Cornus* species and identified interspecies differences in SDH and QDH activities (Nikonorova et al. 2025). Therefore, we propose a broader comparative approach assessing both phytochemical content and enzyme activity across multiple species accumulating different types of tannins. This may provide new insights into the complex regulation of tannin biosynthesis.

The medicinal plants *Hippophae rhamnoides, Astilbe chinensis, Agrimonia pilosa, Agrimonia asiatica* and *Cornus sericea* are known to accumulate the various classes of tannins. For example, various HT such as hippophaenins A and B, peduncalagin, casuarinin, tellimagrandin I, etc. in sea buckthorn and camptothin A and B, cornusiins A, C, D, E, F, G, etc. in red-osier dogwood have been identified (Sheichenko et al. 1987; Yoshida et al. 1991; Nikonorova et al. 2025). In *A. chinensis*, procyanidins with a degree of polymerization of up to four have been reported (Кроль et al. 2025). *Agrimonia* species contain both types of tannins, including pedunculagin, casuarin, procyanidin type B1, procyanidin type B1 dimer, etc (Kashchenko and Olennikov 2020; Wen et al. 2022).

Therefore, the aim of this study was to evaluate the activity SDH, QDH, and PAL, and their influence on the accumulation of different types of tannins in medicinal plants.

# Materials and methods

Fresh leaves of *H. rhamnoides*, *C. sericea*, *A. pilosa*, *A. asiatica*, and *A. chinensis* (Fig. 2) were collected at the Botanical Garden of VILAR, Moscow (Biocollection of VILAR, 55°33'51.8"N 37°35'56.8"E) in six biological replicates and stored at -80°C until evaluation of enzymes activity. For phytochemical analysis, samples were freeze-dried for 72 hours (FreeZone 2.5L, LABCONCO®, USA) and stored at -20°C prior to analysis.

Approximately 1 g of leaf samples was homogenized in 0.2 M Tris-HCl buffer (pH = 7.4) containing 2 mM EDTA, 1 mM PMSF, 1 mM benzamidine, 10 mM dithiothreitol (DTT), 5% PVP, and 3% XAD-4. The supernatant was used for protein precipitation by acetone as described previously (Nikonorova and Baleyev 2023; Nikonorova et al. 2025). Protein content was determined by Bradford method (Bradford 1976). The activity of SDH and QDH was determined spectrophotometrically in purified extract on SPECTROstar NANO (BMG LABTECH, Germany) by the increase in absorbance of NADP + at a wavelength of 340 nm in a reaction with 8 mM shikimic or 20 mM quinic acid at pH = 10.5 and 11.0, respectively (Ossipov et al. 2000; Nikonorova et al. 2025). The activity of PAL was assayed as described by Ertani et al. with modifications (Ertani et al. 2013) by monitoring the formation of trans-cinnamic acid at 290 nm from 40 mM L-phenylalanine (pH = 8.8).

Acetone extract for the determination of phenolic compounds was prepared as described earlier (Krol et al. 2023). The amount of HT was calculated as the content of gallic and ellagic acids formed after hydrolysis with 6N HCl for 72 h, detected with Shimadzu Prominence-I LC-2030C 3D HPLC system equipped with a PDA detector and a Luna® 5µm C18 100A 250×4.6 mm column in gradient mode. PA content was determined using a modified method of Ossipova et al.: water-, organic-soluble (butanol), and insoluble fractions were analyzed in reaction with butanol: hydrochloric acid reagent (95:5 v/v, BH) containing 0.6 mM $Fe^{3+}$ ions (Ossipova et al. 2001). The PA content was expressed as mg of cyanidin-3-glycoside per g of DW.

The obtained data were analyzed using R Studio (version 023.09.1 + 494) and the R programming language (version 4.3.2). For data with non-Gaussian distribution log10 transformation was applied to fit

a Gaussian data distribution. Data were compared using ANOVA followed by Tukey's test. Data were shown as median (25–75) before transformation. Differences were considered significant at $p < 0.05$. Correlation analysis for log10-transformed data was performed by Pearson method.

# Results

As its seen from Table 1, the highest SDH and PAL activities were observed in the leaves of *H. rhamnoides* and *C. sericea*: SDH activity was almost 2–4 times higher than in *A. asiatica*, *A. pilosa*, and *A. chinensis.* The highest PAL activity was observed in *H. rhamnoides* being more than 3-fold higher than in *A. chinensis* ($p = 0.019$), where PAL activity was the lowest (Table 1). Oppositely, leaves of *H. rhamnoides* and *C. sericea* were characterized by the lowest QDH activity. The highest QDH activity was found in *A. chinensis* leaves, being s 3.1 times higher than in *H. rhamnoides* ($p = 0.013$). These data correspond to the results of our previous studies on SDH activity in leaves of *C. sericea* and *H. rhamnoides* (Nikonorova and Baleyev 2023; Nikonorova et al. 2025).

Table 1
SDH, QDH, and PAL activities in the studied species.

| Activity | *C. sericea* | *H. rhamnoides* | *A. asiatica* | *A. pilosa* | *A. chinensis* |
|---|---|---|---|---|---|
| SDH, nkat/mg of protein | 3.15 (2.61–3.47) | 4.86 (4.71–9.95) [3,4,5] | 1.70 (1.67–2.02) [2] | 1.24 (1.19–2.30) [2] | 1.94 (1.46–2.05) [2] |
| QDH, nkat/mg of protein | 2.16 (1.92–3.88) | 1.06 (0.99–1.16) [4,5] | 2.53 (2.11–2.94) | 3.11 (2.47–3.39) [2] | 3.30 (3.01–3.60) [2] |
| PAL, μM *trans*-cinnamic acid/min * mg of protein | 3.59 (2.91–5.95) | 6.26 (6.13–7.58) [5] | 3.47 (2.96–4.78) | 3.25 (2.49–4.10) | 1.90 (0.83–2.83) [2] |

1 – significant difference in comparison to *C. sericea*, $p_{adj} < 0.05$

2 – significant difference in comparison to *H. rhamnoides*, $p_{adj} < 0.05$

3 – significant difference in comparison to *A. asiatica*, $p_{adj} < 0.05$

4 – significant difference in comparison to *A. pilosa*, $p_{adj} < 0.05$

5 – significant difference in comparison to *A. chinensis*, $p_{adj} < 0.05$

The highest total content of PA was found in the leaves of *A. chinensis*, which was 7.5 times higher than in *H. rhamnoides* ($p < 0.001$), and almost 2 times higher than in *A. asiatica* ($p < 0.001$), and *A. pilosa* ($p < 0.001$) (Table 2). No significant differences in total PA were found between the two *Agrimonia* species.

When comparing water-, butanol-, and insoluble fractions, it was found that water-soluble PAs predominated in the all studied species. The highest content of HT was observed in *C. sericea* and *H. rhamnoides.*

Table 2
The total content of HT and PA with fractions in the leaves of studied species.

| Parameter | *C. sericea* | *H. rhamnoides* | *A. asiatica* | *A. pilosa* | *A. chinensis* |
|---|---|---|---|---|---|
| Total HT, mg GA&EA/g DW | 30.37 (30.28–33.03) 3,4,5 | 25.11 (23.33–31.78) 3,4,5 | 7.77 (4.47–14.10) 1,2,5 | 4.65 (3.05–11.99) 1,2,5 | 0.0 (0.0–0.0) 1,2 |
| Total PA, mg C3G/g DW | 0.11 (0-0.38) 2,3,4,5 | 10.37 (10.09–16.70) 1,3,4,5 | 51.03 (44.59–52.85) 1,2 | 44.82 (40.24–54.98) 1,2 | 78.23 (72.09–79.16) 1,2,5 |
| Water-soluble PA, mg C3G /g DW | 0.11 (0.0-0.38) 2,3,4,5 | 10.05 (8.42–12.32) 1,3,4,5 | 36.76 (32.05–37.88) 1,2,5 | 39.75 (33.19–45.84) 1,2,5 | 47.33 (44.49–52.91) 1,2,5 |
| Organic-soluble PA, mg C3G /g DW | 0.0 (0.0–0.0) 3,4,5 | 1.08 (0.78–2.30) 1,3,5 | 8.21 (7.59–9.19) 1,2 | 5.24 (3.70–6.33) 1 | 21.39 (19.69–22.13) 1,2 |
| Insoluble PA, mg C3G /g DW | 0.0 (0.0–0.0) 3,4,5 | 0.0 (0.0-0.08) 3,4,5 | 6.09 (4.06–6.39) 1,2 | 1.03 (0.50–1.21) 1,2 | 6.55 (6.29–8.96) 1,2 |

1 – significant difference in comparison to *C. sericea*, $p_{adj} < 0.05$

2 – significant difference in comparison to *H. rhamnoides*, $p_{adj} < 0.05$

3 – significant difference in comparison to *A. asiatica*, $p_{adj} < 0.05$

4 – significant difference in comparison to *A. pilosa*, $p_{adj} < 0.05$

5 – significant difference in comparison to *A. chinensis*, $p_{adj} < 0.05$

The correlation analysis between the content of tannins and enzyme activities revealed the moderate and weak correlations with opposing directions for PA and HT. A significant positive correlation between SDH activity and HT content was found (Fig. 3A). There was no correlation of QDH and PAL activity with tannins content (Fig. 3C, D, E, F).

# Discussion

There are relatively few studies on the relationships between the content of different types of tannins and enzyme activities. The most of the studies are aimed at identifying changes in one family or genus of medicinal and aromatic plants and, more often, in response to some stress factor (Díaz et al. 2001; Bontpart et al. 2016; Huang et al. 2019; Habashi et al. 2019). Here we are presenting the results of a comparative study involving five species, accumulating different types of tannins.

In present study, the correlation analysis between the content of tannins and enzyme activities revealed moderate and weak correlations with opposing directions. It is known that many plants contain several isoforms of SDH with different activities, and not all of them possess SDH and gallate-forming activity. For example, grapevine has four SDH genes: VvSDH1 shows high “classical” SDH activity, whereas VvSDH3 and VvSDH4 exhibit lower shikimate-forming activity but are capable to produce gallic acid (Bontpart et al. 2016). At the same time, the transgene expressing VvSDH3 was characterized by an increase not only in the synthesis of aromatic amino acids, hydroxycinnamic acids and flavan-3-ols (precursors of PA), but also gallic acid, β-glucogallin, galloylated flavan-3-ols (Bontpart et al. 2016). Tea plants also possess multiple DQD/SDH genes: one encodes a typical shikimate-forming enzyme, while others are specialized for supplying gallic acid used in galloylated catechins (Jiang et al. 2013; Huang et al. 2019). This functional diversification – gallate-producing vs. shikimate-producing SDHs – means that different isoforms may channel carbon toward HT rather than PA and vice versa. In the present study, SDH activity positively correlated with HT levels, reflecting that carbon flux is directed toward the gallic acid route (high SDH activity favoring HTs), with less of it available for the phenylpropanoid and PA synthesis.

Another branch-point in shikimate pathway is at 3-DHQ, one step earlier in the shikimate pathway. According to available data, QDH, the SDH paralogue, can compete with the DQD/SDH route, reducing 3-DHQ to quinate instead of its dehydration to 3-DHS, and preventing entry of carbon to both downstream routes (shikimate/phenylpropanoids/PA and gallic acid) (Carrington et al. 2018; Gritsunov et al. 2018; Carrington, Yuriko 2020). Quinate itself doesn’t form tannins, but it can be used to produce chlorogenic acid when coupled with the phenylpropanoid pathway (Reine Judesse Soviguidi et al. 2022). Therefore, it may allow plants to differentially regulate which SDH (or QDH) variant is active based on developmental or environmental context, thereby channeling metabolites appropriately. In present study, QDH activity did not correlate with the tannins content. Consequently, it mostly controls quinate metabolism, which may reflect physiological status, not specialized metabolite synthesis: the available data show, that quinate levels and QDH activity are decreased during fruits maturation (Marsh et al. 2009; Jiang et al. 2020). However, there are limited data on QDH activity in leaves.

Although PAL is mostly linked to PA and flavonoid synthesis, there was no correlation between PAL activity and PA content. In plants, PA biosynthesis diverges downstream of PAL, requiring additional steps like chalcone synthase, dihydroflavonol-4-reductase, leucoanthocyanidin reductase, and anthocyanidin reductase (Mora et al. 2022). Therefore, PAL activity alone doesn't determine PA levels – it's too upstream and nonspecific. PAs may be regulated more by later enzymes or transcription factors (like MYB-bHLH-WD40 complexes). Also, the inhibition of PAL by the caffeic and gallic acids (Sato et al.

1982), flavonoids (Sato and Sankawa 1983), and product of reaction – *t*-cinnamic acid (O'Neal and Keller 1970) was shown, which may explain the absence of correlation between PAL and tannins content (Schaart et al. 2013; Liu et al. 2018). Species like *A. chinensis* might accumulate high levels of PA due to strong regulation of downstream flavonoid-specific enzymes, even if PAL activity is moderate.

The limitations of this study were a relatively small sample size due to the labor-intensive extraction process and lack of reliable data on isoforms of DQD/SDH in the studied species.

Overall, in present study

1) Evaluation of SDH, QDH, and PAL activity was carried out in five plant species accumulating different types of tannins;

2) The highest level of PA was found in *A. sinensis* with water-soluble PAs predominated in the all studied species. The highest level of HT was observed in *C. sericea* and *H. rhamnoides* leaves;

3) Significant correlation of SDH activity and HT content was found, while there was no relationship between QDH and PAL activity and tannins content.

The data obtained showed a relationship between the activity of SDH and the content of HT. However, given the limited data on the activity of other tannin synthesis enzymes and the possible presence of different isoforms, it is impossible to draw confident conclusions.

## Declarations

# Conflicts of interest

The authors declare no conflict of interest.

# Institutional review board statement

Not applicable.

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# Data availability

Data will be made available on request.

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# Figures

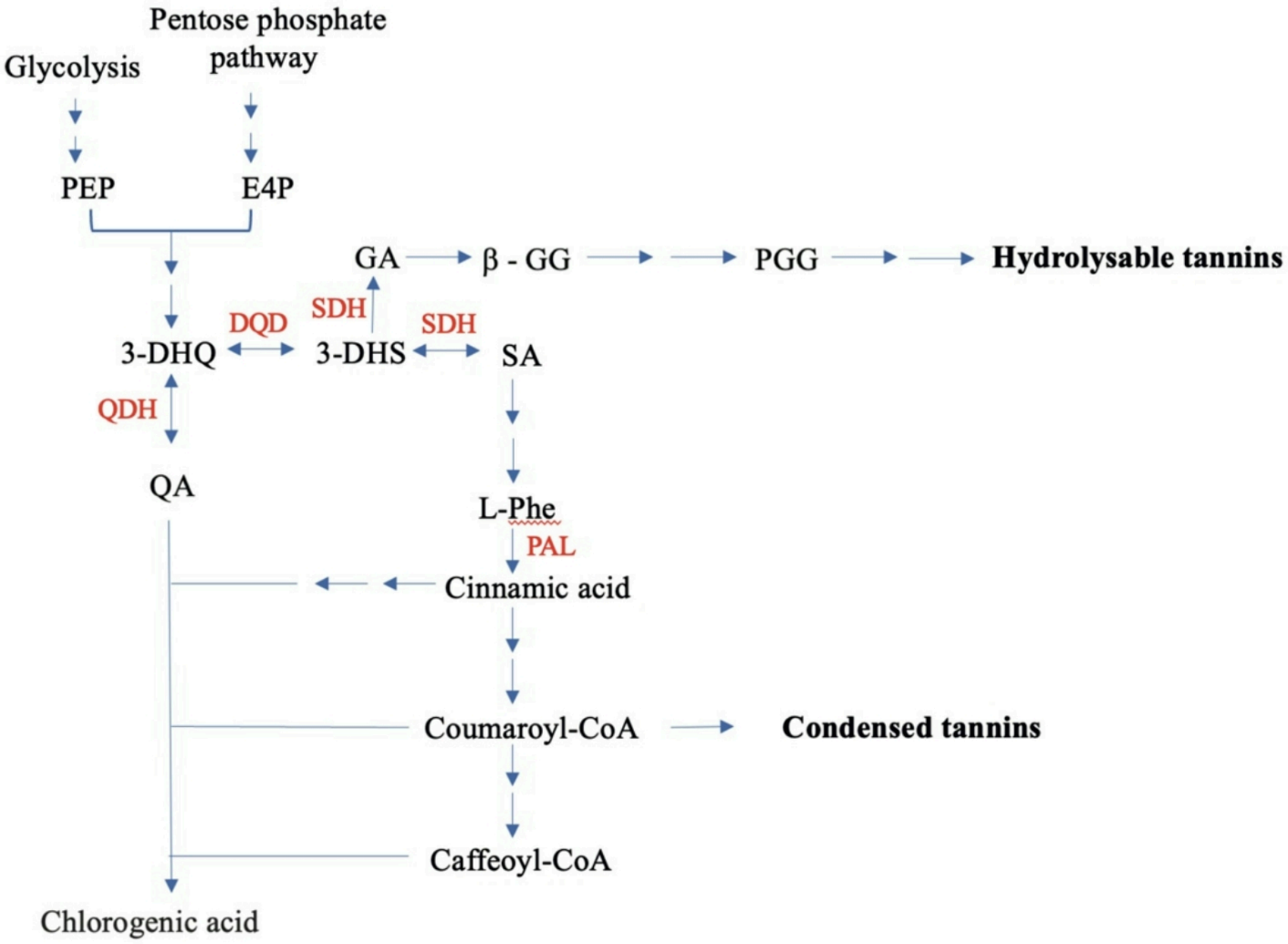
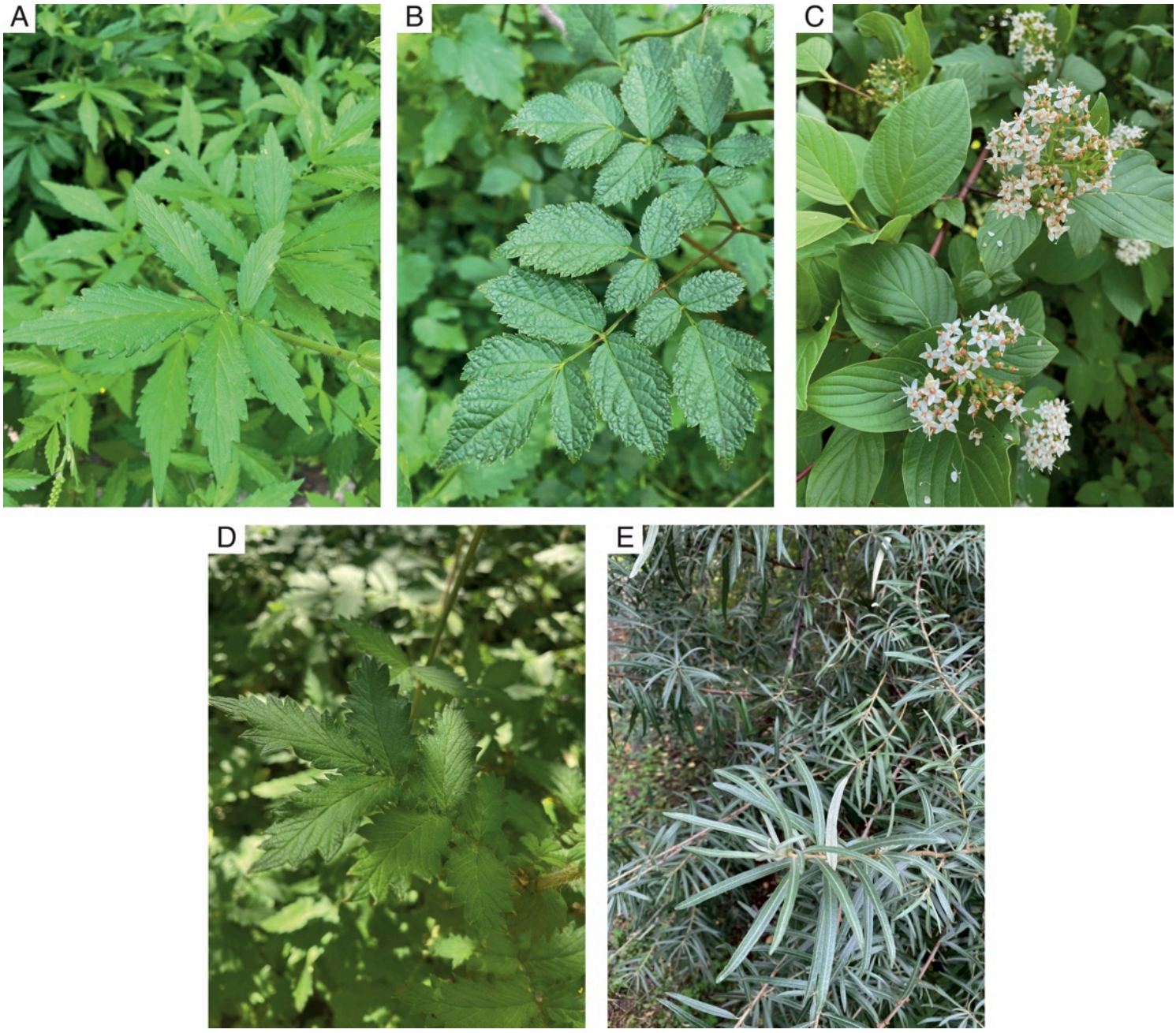



**Figure 1**

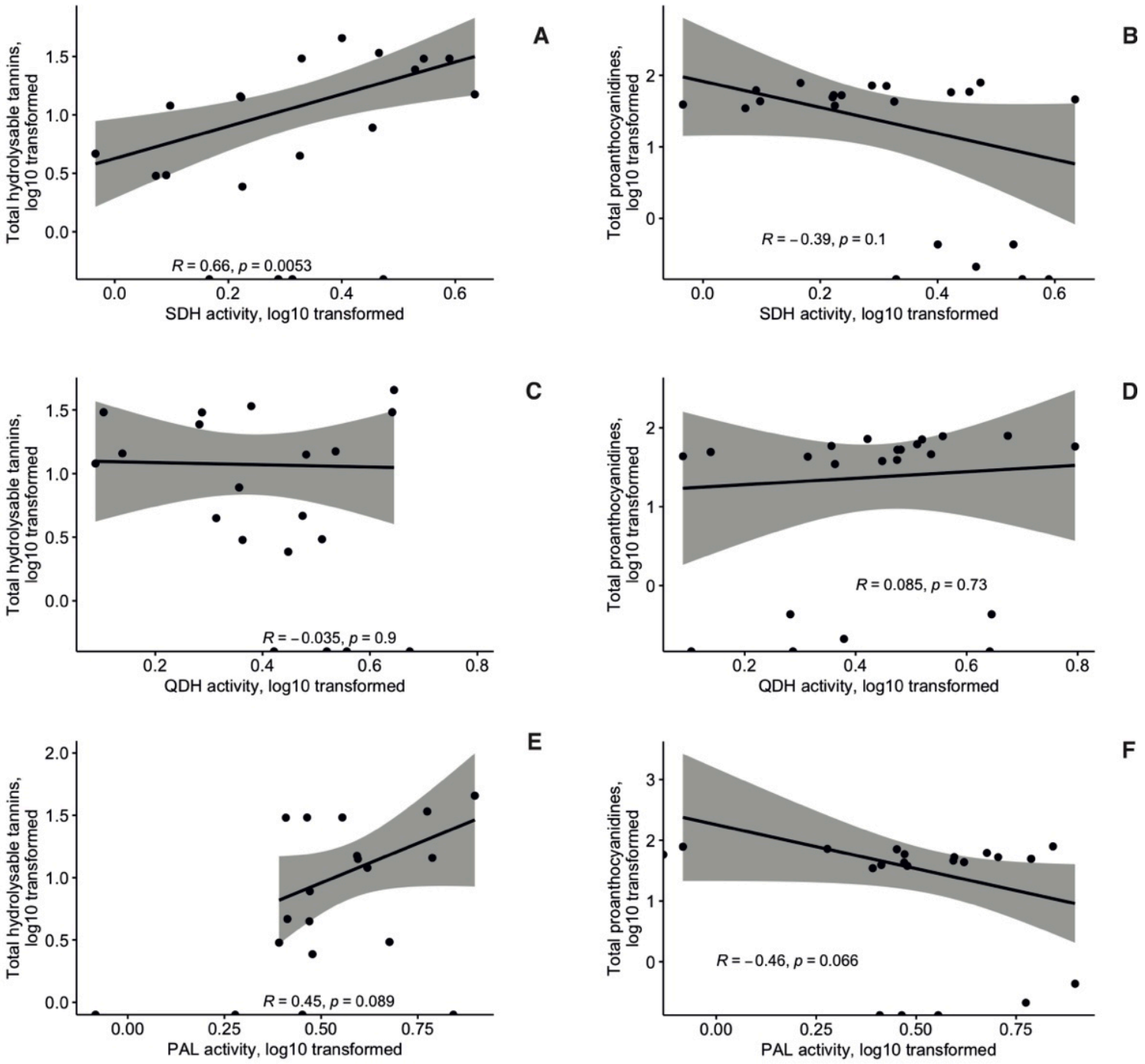
The short scheme of HT and PA biosynthesis with the relationships between key enzymes and intermediates.

Abbr.: PEP – phosphoenolpyruvate, E4P – erythrose-4-phosphate, 3-DHQ – 3-dehydroquinate, 3-DHS – 3-dehydroshikimate, SA – shikimic acid, QA – quinic acid, L-Phe – L-phenylalanine, GA – gallic acid, β-GG – β-glucogallin, PGG – penthagalloylglycose; DQD – dehydroquinate dehydratase, SDH – shikimate dehydrogenase, QDH – quinate dehydrogenase, PAL – phenylalanine ammonia lyase.




## Figure 2

Leaves of six species used in present study: A – *A. pilosa,  B – A. chinensis, C – C. sericea, D – A. asiatica E – H. rhamnoides.*




## Figure 3

Correlation analysis between enzyme activities and the HT and PA content in the studied species.