

ABSTRACT

Floral scent is an essential and genetically complex trait in herbaceous peonies (*Paeonia lactiflora* Pall.); however, specific genes related to metabolic and regulatory networks remain scantily studied. Our study integrated metabolite profiling and RNA-sequencing to screen floral scent biosynthetic genes. Hence, the major molecules identified by headspace collection combined with cultivar-specific GC-MS analysis were geraniol, β -caryophyllene, 2-phenylethanol (2-PE), citronellol, and 1,8-cineole. Genes related to terpenoids and 2-PE biosynthesis were identified after the assembly and annotation of the *P. lactiflora* transcriptomes. Eight angiosperm-specific terpene synthases (TPSs) from the TPS-a and TPS-b clades, as well as enzymes linked to 2-PE synthesis such as aromatic amino acid decarboxylase (AADC), phenylacetaldehyde reductase (PAR), and geraniol reductase (GER) were identified. The biochemical analysis of the enzymes encoded by *PIPAR1* and *PIGER1* generated 2-PE from phenylacetaldehyde (PAld). The pairwise alignment of *AADC1* reveals a splice variant lacking a 124 bp fragment, thus highlighting the possible role of alternative splicing in modulating floral scent composition. This study offers insights into the molecular-level biosynthesis of terpenoids and 2-PE in *Peonia* taxa, and provides the basis for the functional characterization, breeding, and bioengineering of prospective candidate genes for the production of floral volatiles in the *Paeonia* genus.