

*Article*

# **Distribution of protein precipitation capacity within variable proanthocyanidin fingerprints**

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**Table S1.** The plant species and tissues used in this study. The plant sources are similar as utilised in Leppä *et al.* [17].

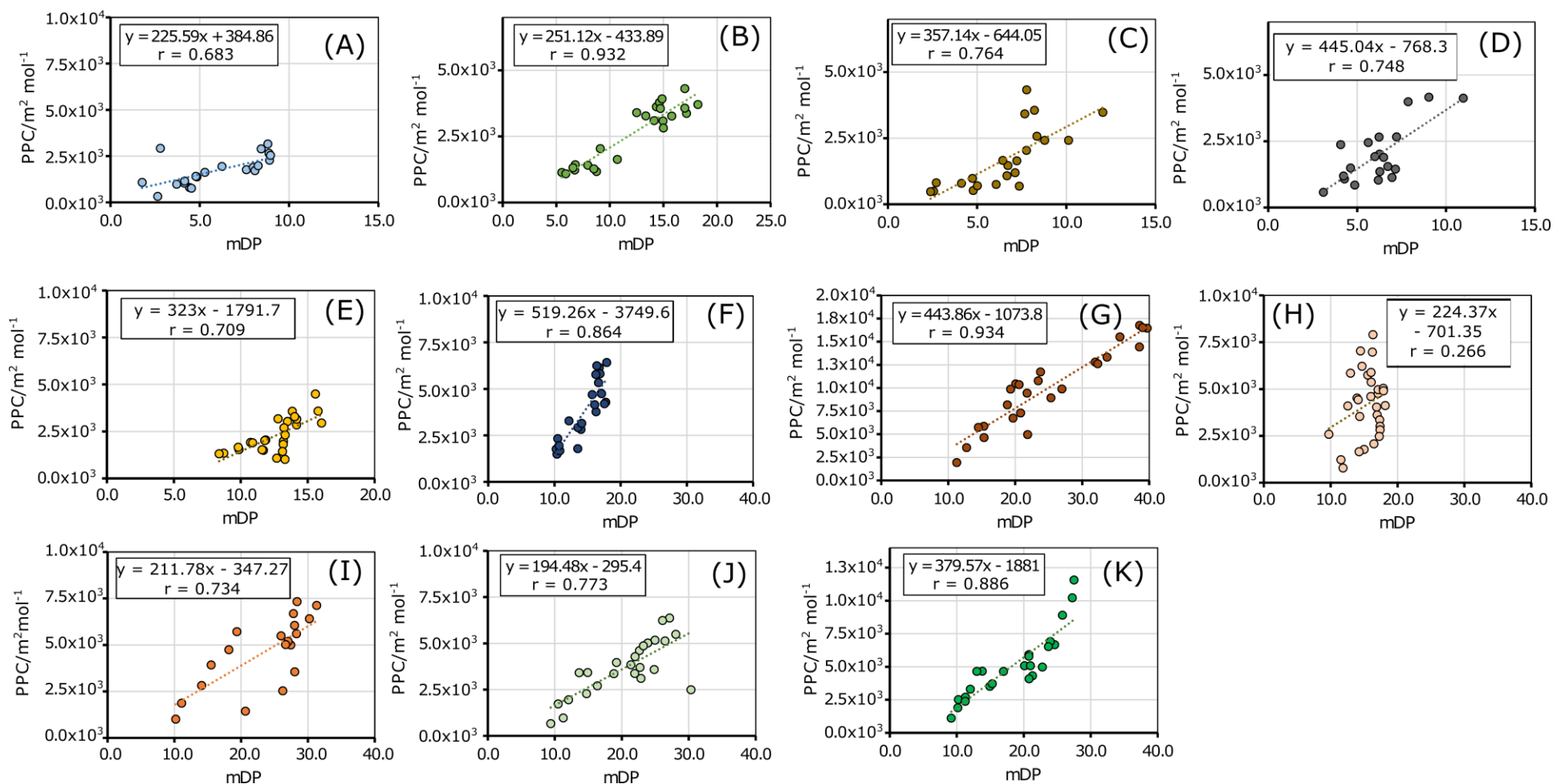
Plant species		Semipreparative source material		
Latin name	Plant tissue	<sup>a</sup> mDP	<sup>b</sup> PC/PD ratio	<sup>c</sup> EG (mol/mol)
<i>Aesculus hippocastanum</i> L.	leaves	4	99/1	-
<i>Trifolium medium</i> L.	flowers	9	99/1	-
<i>Rhododendron dichroanthum</i> Diels.	leaves	5	79/21	1.0
<i>Rhododendron schlippenbachii</i> Maxim.	leaves	6	78/22	1.3
<i>Larix</i> sp	needles	12	62/38	-
<i>Lotus corniculatus</i> L.	green brownish pods	14	45/55	-
<i>Lysimachia vulgaris</i> L.	flowers	20	27/73	-
<i>Pinus sylvestris</i> L.	needles	18	24/76	-
<i>Salix phylicifolia</i> L.	leaves	20	15/85	-
<i>Ribes alpinum</i> L.	leaves	19	3/97	-
<i>Trifolium repens</i> L.	flowers	18	2/98	-

<sup>b</sup>Mean degree of polymerization (mDP) and <sup>b</sup>ratio of procyanidin and prodelphinidin subunits (PC/PD) measured by UPLC-MS/MS [31]. <sup>c</sup>The estimate of the relative galloyl content to proanthocyanidin content.

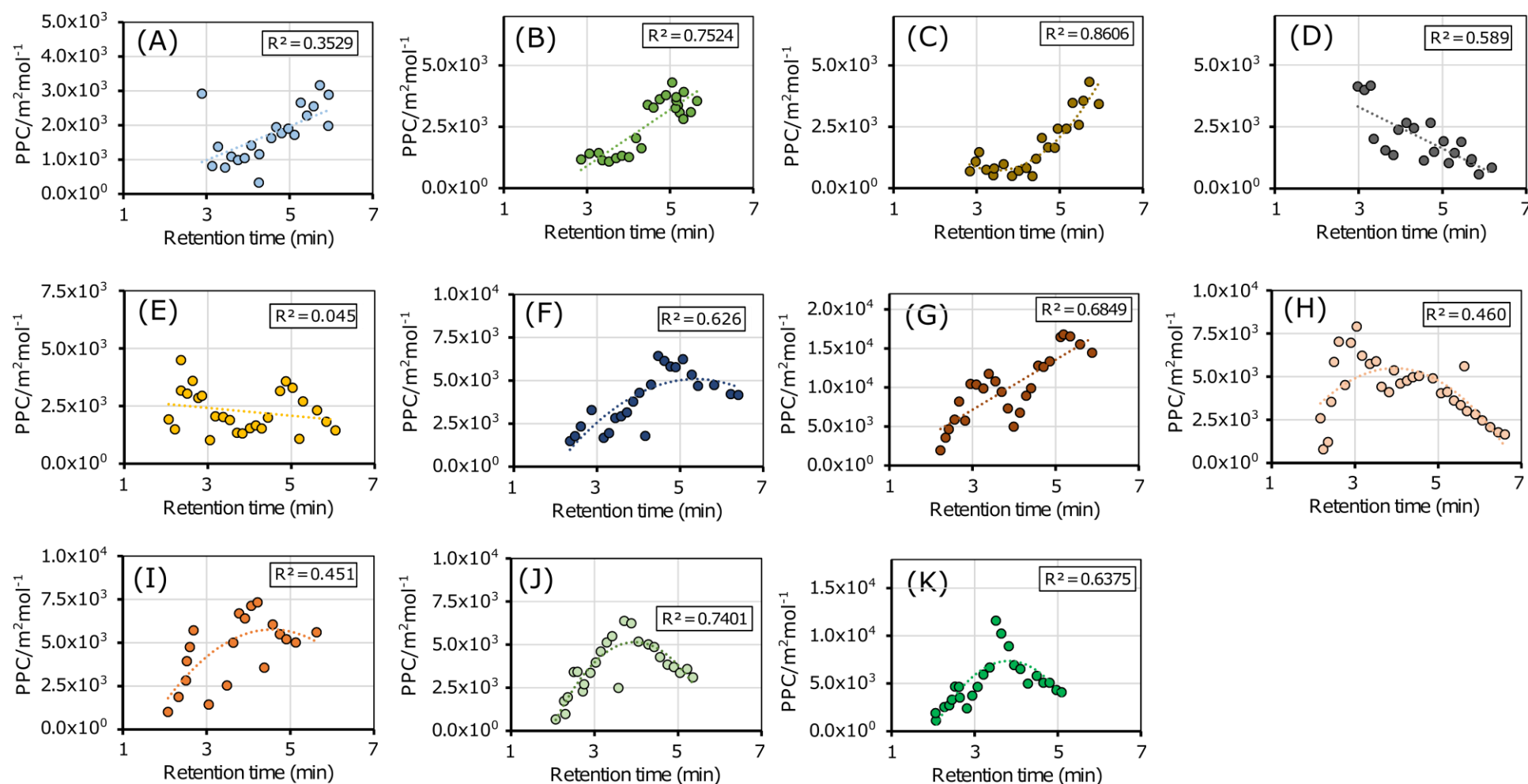
**Table S1.** The non-standardised Partial Least Squares Regression coefficients of each plant species.

Plant species	Variable	Non-standardized Regression coefficients	Plant species	Variable	Non-standardized Regression coefficients
<i>A. hippo-castanum</i>	Intercept	−615.81	<i>L. vulgaris</i>	Intercept	−8467.20
	$t_R$	262.16		$t_R$	1 489.18
	mDP	166.94		mDP	358.43
	PD-%	135.15		PD-%	60.38
<i>T. medium</i>	Intercept	−1 688.00	<i>P. sylvestris</i>	Intercept	3 059.66
	$t_R$	527.58		$t_R^2$	−78.51
	mDP	155.63		$t_R$	−521.90
	PD-%	22.49		mDP	512.87
<i>R. dichro-anthum</i>	Intercept	−2 468.60	<i>S. phyllicifolia</i>	PD-%	−43.16
	$t_R^2$	50.85		Intercept	7 605.46
	$t_R$	359.30		$t_R^2$	−4.99
	mDP	233.20		$t_R$	50.58
	PD-%	8.49		mDP	109.31
<i>R. schlippenbachii</i>	EG	−77.49		PD-%	−69.79
	Intercept	1 403.34	<i>R. alpinum</i>	Intercept	38432.80
	$t_R$	−266.09		$t_R^2$	−28.88
	mDP	172.89		$t_R$	−66.94
	PD-%	21.27		mDP	114.94
	EG	140.09		PD-%	−380.54
<i>Larix</i> sp.	Intercept	−1477.70	<i>T. repens</i>	Intercept	2 276.75
	$t_R$	−35.96		$t_R^2$	−122.33
	mDP	296.12		$t_R$	−413.05
	PD-%	3.43		mDP	510.33
<i>L. corniculatus</i>	PD-%	50.40		PD-%	−37.49
	Intercept	−7 837.30			
	$t_R^2$	7.48			
	$t_R$	219.88			
	mDP	559.32			

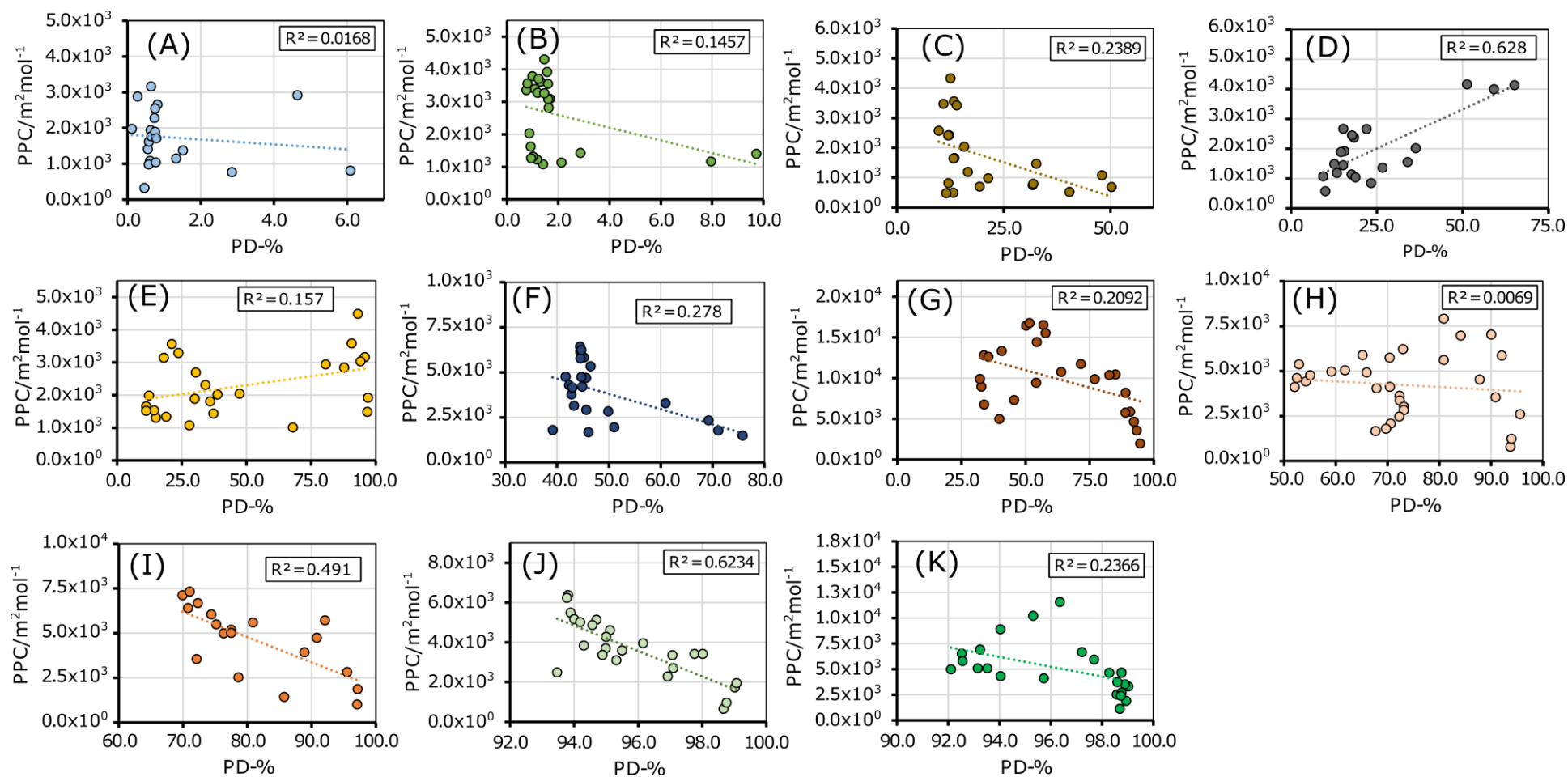
Abbreviations used: mean degree of polymerization (mDP), retention time ( $t_R$ ), quadratic term of retention time ( $t_R^2$ ), proportion of prodelphinidin (PD-%) and the estimated galloyl content in relation to proanthocyanidin content (EG, mol/mol).



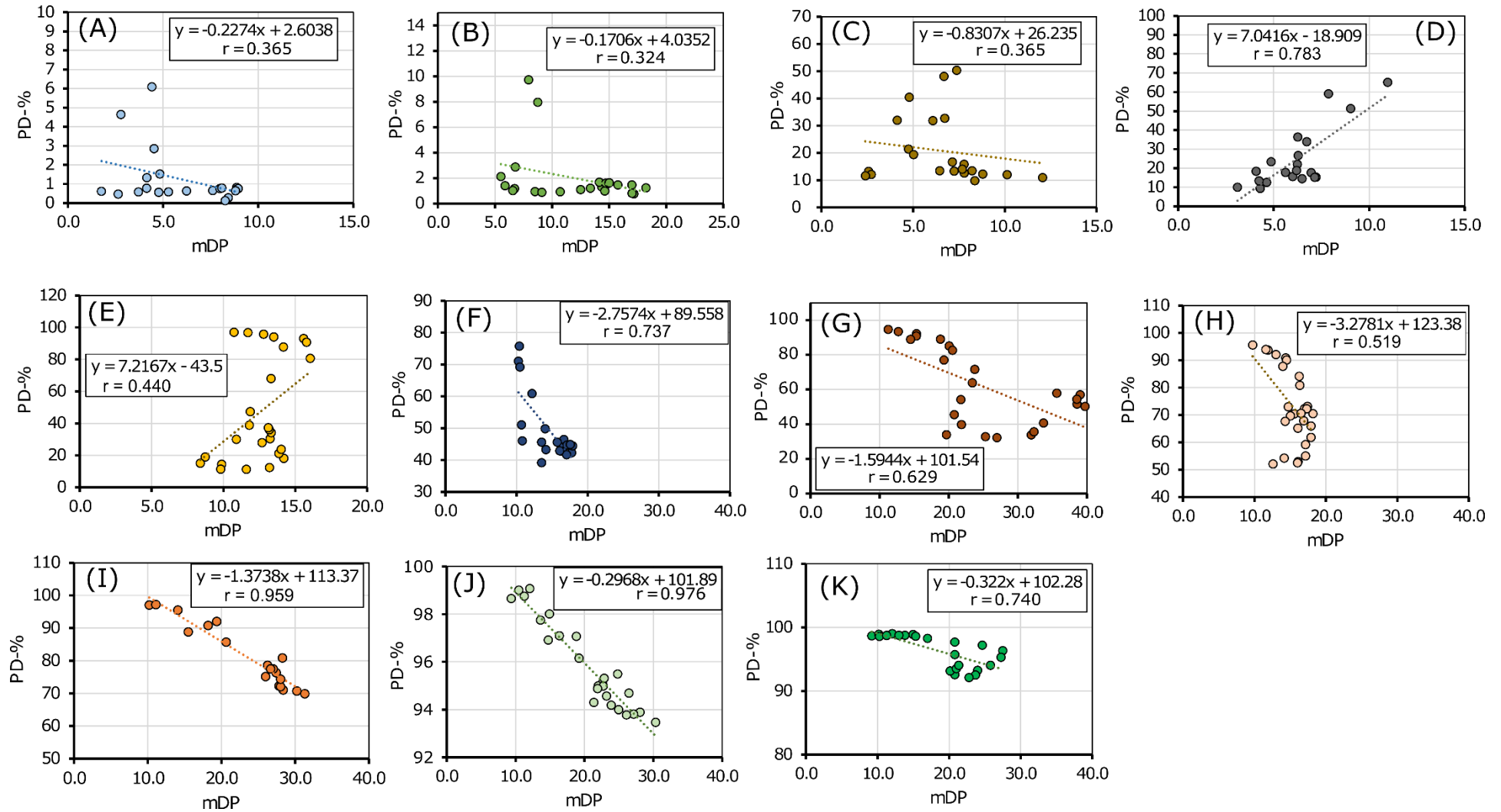
**Figure S1.** Protein precipitation capacity (PPC) as a function of mean degree of polymerization (mDP) of (A) *Aesculus hippocastanum*, (B) *Trifolium medium*, (C) *Rhododendron dichroanthum*, (D) *Rhododendron schlippenbachii*, (E) *Larix* sp, (F) *Lotus corniculatus*, (G) *Lysimachia vulgaris*, (H) *Pinus sylvestris*, (I) *Salix phylicifolia*, (J) *Ribes alpinum* and (K) *Trifolium repens*.



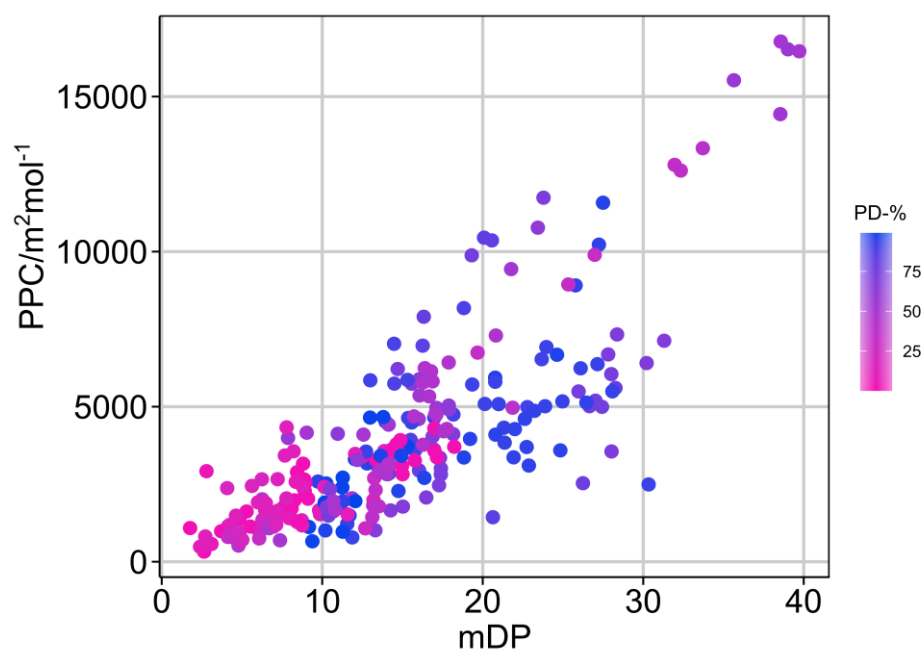
**Figure S2.** Protein precipitation capacity (PPC) as a function of retention time of (A) *Aesculus hippocastanum*, (B) *Trifolium medium*, (C) *Rhododendron dichroanthum*, (D) *Rhododendron schlippenbachii*, (E) *Larix* sp, (F) *Lotus corniculatus*, (G) *Lysimachia vulgaris*, (H) *Pinus sylvestris*, (I) *Salix phylicifolia*, (J) *Ribes alpinum* and (K) *Trifolium repens*.



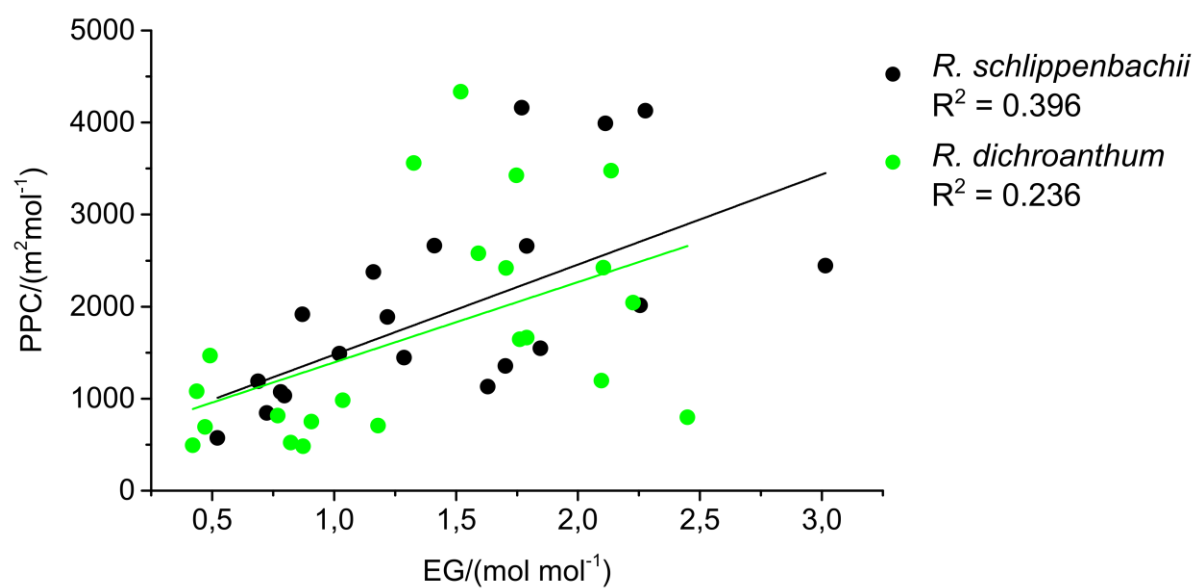
**Figure S3.** Protein precipitation capacity (PPC) as a function of prodelphinidin proportion (PD-%) of (A) *Aesculus hippocastanum*, (B) *Trifolium medium*, (C) *Rhododendron dichroanthum*, (D) *Rhododendron schlippenbachii*, (E) *Larix* sp, (F) *Lotus corniculatus*, (G) *Lysimachia vulgaris*, (H) *Pinus sylvestris*, (I) *Salix phylicifolia*, (J) *Ribes alpinum* and (K) *Trifolium repens*.



**Figure S4** Prodelphinidin proportion (PD-%) as a function of the mean degree of polymerization (mDP) of (A) *Aesculus hippocastanum*, (B) *Trifolium medium*, (C) *Rhododendron dichroanthum*, (D) *Rhododendron schlippenbachii*, (E) *Larix* sp, (F) *Lotus corniculatus*, (G) *Lysimachia vulgaris*, (H) *Pinus sylvestris*, (I) *Salix phylicofilia*, (J) *Ribes alpinum* and (K) *Trifolium repens*.

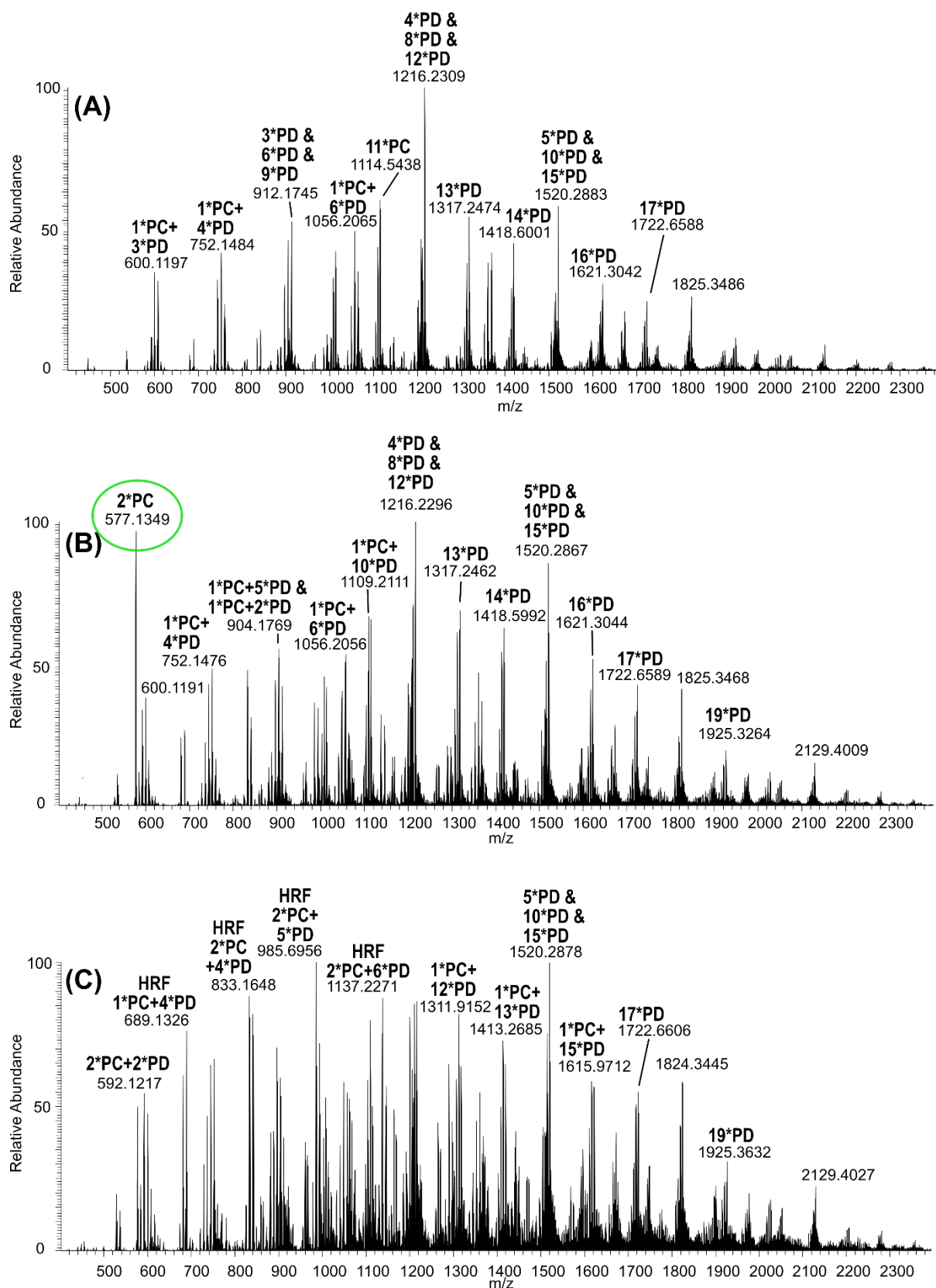


**Figure S5.** Protein precipitation capacity (PPC) as a function of the mDP. The colour gradient illustrates the PD-% of the fractions ranging from PC pure (pink) to PD pure (blue).



**Figure S6.** Protein precipitation capacity (PPC) as a function of the estimation of the relative galloyl content (EG).





**Figure S7.** High-resolution mass spectra of *Ribes alpinum* semipreparative fraction numbers (A) 64, (B) 68 and (C) 72. Compound interpretations are presented above each signal. For instance “2\*PC+2\*PD” means a tetrameric proanthocyanidin consisting from two procyanidin units and two prodelphinidin units. All identified compounds were B-type proanthocyanidins consisting from procyanidins and prodelphinidins. The used abbreviations are as follows: PC = procyanidin, PD = prodelphinidin, HRF = heterocyclic ring fission.