

## SUPPLEMENTARY MATERIALS

# Partition coefficient ( $\log P$ ) of hydrolysable tannins

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**Table S1.** Purity of hydrolysable tannins studied, English and latin names and plant part used of the original plant material.

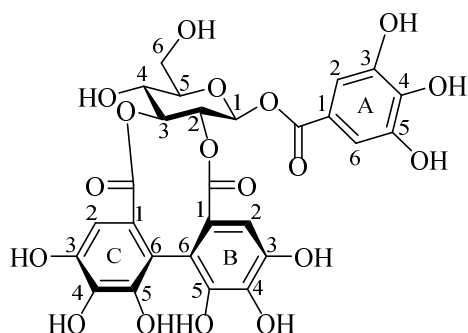
#	Hydrolysable Tannin	Purity-% <sup>a</sup>	Plant Origin		
			English Name	Latin Name	Plant Part
1	1- <i>O</i> -galloyl- $\beta$ - <i>D</i> -glucose	87.9 %	-	-	-
2	1,6-di- <i>O</i> -galloyl- $\beta$ - <i>D</i> -glucose	99.9 %	Meadowsweet	<i>Filipendula ulmaria</i>	flower
3	corilagin	98.3 %	Black myrabolan	<i>Terminalia chebula</i>	leaf
4	isostrictinin	93.4 %	Sea buckthorn	<i>Hippophae rhamnoides</i>	leaf
5	strictinin	98.6 %	Sea buckthorn	<i>Hippophae rhamnoides</i>	leaf
6	1,2,6-tri- <i>O</i> -galloyl- $\beta$ - <i>D</i> -glucose	93.1 %	Sea buckthorn	<i>Hippophae rhamnoides</i>	leaf
7	chebularin	97.0 %	Black myrabolan	<i>Terminalia chebula</i>	leaf
8	casuariin	92.0 %	Sea buckthorn	<i>Hippophae rhamnoides</i>	leaf
9	pedunculagin	98.8 %	Silverweed	<i>Argentina anserina</i>	leaf
10	tellimagrandin I	94.8 %	Meadowsweet	<i>Filipendula ulmaria</i>	flower
11	1,2-di- <i>O</i> -galloyl-4,6-HHDP- $\beta$ - <i>D</i> -glucose	95.0 %	Meadowsweet	<i>Filipendula ulmaria</i>	flower
12a	1,2,3,6-tetra- <i>O</i> -galloyl- $\beta$ - <i>D</i> -glucose <sup>b</sup>	71.4 %	Norway maple	<i>Acer platanoides</i>	leaf
12b	1,2,4,6-tetra- <i>O</i> -galloyl- $\beta$ - <i>D</i> -glucose <sup>b</sup>	74.7 %	Norway maple	<i>Acer platanoides</i>	leaf
13	castalagin	99.6 %	English oak	<i>Quercus robur</i>	acorn
14	vescalagin	97.0 %	English oak	<i>Quercus robur</i>	acorn
15	casuarictin	97.5 %	Meadowsweet	<i>Filipendula ulmaria</i>	flower
16	casuarinin	97.5 %	Sea buckthorn	<i>Hippophae rhamnoides</i>	leaf
17	stachyurin	96.8 %	Sea buckthorn	<i>Hippophae rhamnoides</i>	leaf
18	tellimagrandin II	90.2 %	Meadowsweet	<i>Filipendula ulmaria</i>	flower
19	1,2,3,4,6-penta- <i>O</i> -galloyl- $\beta$ - <i>D</i> -glucose <sup>b</sup>	98.6 %	-	-	-
20	geraniin	84.8 %	Wood cranesbill	<i>Geranium sylvaticum</i>	leaf
21	carpinusin	98.3 %	Wood cranesbill	<i>Geranium sylvaticum</i>	leaf
22	chebulagic acid	96.1 %	Black myrabolan	<i>Terminalia chebula</i>	leaf
23	chebulinic acid	88.3 %	Black myrabolan	<i>Terminalia chebula</i>	leaf
24	grandinin	98.3 %	-	-	-
25	punicalagin	98.4 %	Black myrabolan	<i>Terminalia chebula</i>	leaf
26	hexagalloylglucose	94.1 %	Norway maple	<i>Acer platanoides</i>	leaf
27	castavalonic acid	91.7 %	English oak	<i>Quercus robur</i>	acorn

#	Hydrolysable Tannin	Purity-% <sup>a</sup>	Plant Origin		
			English Name		
28	vescavalonic acid	97.6 %	English oak	<i>Quercus robur</i>	acorn
29	hippohaenin B	99.9 %	Sea buckthorn	<i>Hippophae rhamnoides</i>	leaf
30	hippohaenin C	96.2 %	Sea buckthorn	<i>Hippophae rhamnoides</i>	leaf
31	heptagalloylglucose	97.2 %	Norway maple	<i>Acer platanoides</i>	leaf
32	octagalloylglucose	96.8 %	Norway maple	<i>Acer platanoides</i>	leaf
33	gallotannin mixture	97.8 %	Norway maple	<i>Acer platanoides</i>	leaf
34	oenothein B	93.1 %	Willowherb	<i>Chamaenerion angustifolium</i>	leaf
35	rosenin C	94.2 %	Raspberry	<i>Rubus idaeus</i>	leaf
36	rugosin E	91.2 %	Meadowsweet	<i>Filipendula ulmaria</i>	flower
37	cocciferin D <sub>2</sub>	93.0 %	English oak	<i>Quercus robur</i>	acorn
38	salicarinin A	96.0 %	Purple loosestrife	<i>Lythrum salicaria</i>	leaf
39	salicarinin B	75.2 %	Purple loosestrife	<i>Lythrum salicaria</i>	leaf
40	agrimoniin	97.6 %	Silverweed	<i>Argentina anserina</i>	leaf
41	sanguiin H-6	97.1 %	Raspberry	<i>Rubus idaeus</i>	leaf
42	gemin A	96.9 %	herb Bennet	<i>Geum urbanum</i>	leaf
43	rugosin D	90.7 %	Meadowsweet	<i>Filipendula ulmaria</i>	flower
44	oenothein A	84.5 %	Willowherb	<i>Chamaenerion angustifolium</i>	leaf
45	lambertianin C	98.2 %	Raspberry	<i>Rubus idaeus</i>	leaf
46	rugosin G	90.3 %	Meadowsweet	<i>Filipendula ulmaria</i>	flower-

<sup>a</sup> Purity measured with the UPLC described in Materials and methods and determined at UV 280±1 nm.

<sup>b</sup> Largest impurity in 1,2,3,6-tetra-*O*-galloyl-β-*D*-glucose was 1,2,4,6-tetra-*O*-galloyl-β-*D*-glucose and vice versa.

<sup>c</sup> 1,2,3,4,6-penta-*O*-galloyl-β-*D*-glucose prepared via methanolysis of tannic acid.

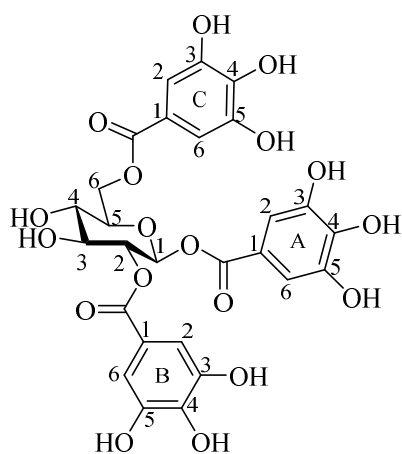


**Figure S1.** Chemical structure of isostrictinin with numbering and definition of rings.

**Table S2.** NMR chemical shifts and coupling constants for isostrictinin. Measured with Bruker Avance-III 500 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Okuda et al. [1].

Position	$\delta^{13}\text{C}/\text{ppm}$	$\delta^1\text{H}/\text{ppm}$	multiplicity	$J_{\text{H,H}}/\text{Hz}$
1	92.24	6.12	d	8.50
2	75.51	5.00	t	9.05
3	80.46	5.20	t	9.53
4	67.96	3.96	t	9.55
5	79.05	3.73	ddd	1.87; 4.37; 9.40
6	61.86	3.81	dd	1.78; 12.18
		3.91	dd	4.63; 11.98
C=O (A)	169.55	-	-	-
A-1	120.22	-	-	-
A-2	110.26	7.16	s	-
A-3	146.30	-	-	-
A-4	139.75	-	-	-
A-5	146.30	-	-	-
A-6	110.26	7.16	s	-
C=O (B)	168.85	-	-	-
B-1	127.22	-	-	-
B-2	114.53	6.43	s	-
B-3	145.14/145.33 <sup>a</sup>	-	-	-
B-4	136.25	-	-	-
B-5	144.42/144.52 <sup>b</sup>	-	-	-
B-6	107.80	6.43	s	-
C=O (C)	165.08	-	-	-
C-1	126.69	-	-	-
C-2	114.53	6.71	s	-
C-3	145.14/145.33 <sup>a</sup>	-	-	-
C-4	136.40	-	-	-
C-5	144.42/144.52 <sup>b</sup>	-	-	-
C-6	107.24	6.71	s	-

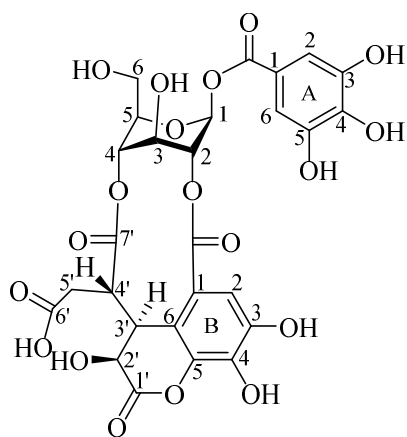
<sup>a</sup>&<sup>b</sup> Assignations may be interchangeable and cannot be verified without further measurements.



**Figure S2.** Chemical structure of 1,2,6-tri-*O*-galloyl- $\beta$ -*D*-glucose with numbering and definition of rings.

**Table S3.** NMR chemical shifts and coupling constants for 1,2,6-tri-*O*-galloyl- $\beta$ -*D*-glucose. Measured with Bruker Avance-III 500 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Nonaka et al. [2].

Position	$\delta^{13}\text{C}/\text{ppm}$	$\delta^1\text{H}/\text{ppm}$	multiplicity	$J_{\text{H,H}}/\text{Hz}$
1	94.08	5.99	d	8.40
2	74.37	5.25	dd	8.58; 9.72
3	76.06	3.98	t	9.20
4	71.63	3.76	t	9.33
5	76.56	3.92	ddd	1.88; 4.55; 9.78
6	64.38	4.58	dd	1.83; 12.13
		4.48	dd	4.62; 12.13
C=O (A)	165.61	-	-	-
A-1	120.81	-	-	-
A-2	110.75	7.07	s	-
A-3	146.53	-	-	-
A-4	140.02	-	-	-
A-5	146.53	-	-	-
A-6	110.75	7.07	s	-
C=O (B)	166.43	-	-	-
B-1	121.98	-	-	-
B-2	110.62	7.10	s	-
B-3	146.41	-	-	-
B-4	139.41	-	-	-
B-5	146.41	-	-	-
B-6	110.62	7.10	s	-
C=O (C)	167.11	-	-	-
C-1	122.15	-	-	-
C-2	110.45	7.15	s	-
C-3	146.54	-	-	-
C-4	139.37	-	-	-
C-5	146.54	-	-	-
C-6	110.45	7.15	s	-

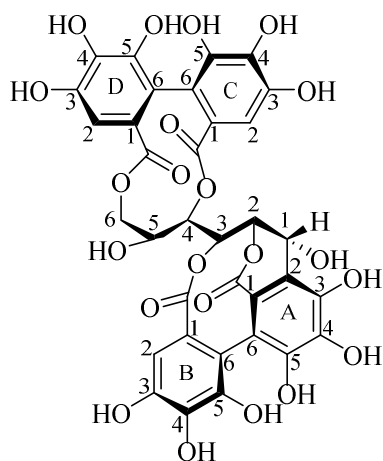


**Figure S3.** Chemical structure of chebulanin with numbering and definition of rings.

**Table S4.** NMR chemical shifts and coupling constants for chebulanin. Measured with Bruker Avance-III 500 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Luo et al. [3].

Position	$\delta^{13}\text{C/ppm}$	$\delta^1\text{H/ppm}$	multiplicity	$J_{\text{H,H/Hz}}$
1	92.61	6.36	d	2.85
2	74.07	5.24	brs	-
3	61.82	4.83	brs	-
4	71.85	4.89	brd	3.35
5	79.26	4.31	t	6.00
6	63.26	4.14	brt	8.20
		4.01	dd	5.43; 11.08
1'	169.70	-	-	-
2'	66.79	4.94	dd	3.85; 7.20
3'	41.09	5.19	dd	1.40; 7.20
4'	39.58	3.90	ddd	1.34; 4.89; 10.21
5'	30.32	2.20	d	1.55
		2.18	d	7.05
6'	172.60 <sup>a</sup>	-	-	-
7'	174.03 <sup>a</sup>	-	-	-
C=O (A)	165.11	-	-	-
A-1	120.91	-	-	-
A-2	110.40	7.20	s	-
A-3	146.27 <sup>b</sup>	-	-	-
A-4	139.60 <sup>b</sup>	-	-	-
A-5	146.27	-	-	-
A-6	110.40	7.20	s	-
C=O (B)	165.95	-	-	-
B-1	119.81	-	-	-
B-2	117.17	7.50	s	-
B-3	146.58	-	-	-
B-4	139.30	-	-	-
B-5	141.16	-	-	-
B-6	116.15	-	-	-

<sup>a</sup> & <sup>b</sup> Assignations may be interchangeable and cannot be verified without further measurements.



**Figure S4.** Chemical structure of casuariin with numbering and definition of rings.

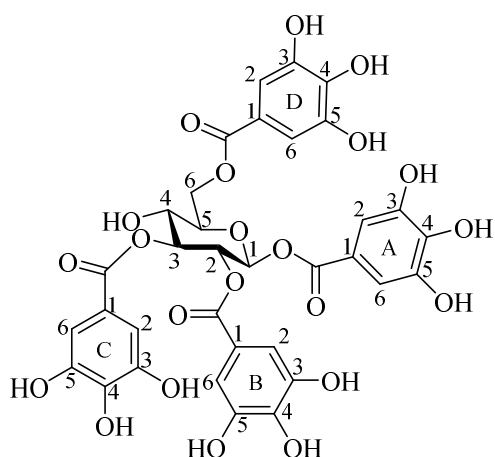
**Table S5.** NMR chemical shifts and coupling constants for casuariin. Measured with Bruker Avance-III 500 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Okuda et al. [4].

Position	$\delta^{13}\text{C}/\text{ppm}$	$\delta^1\text{H}/\text{ppm}$	multiplicity	$J_{\text{H,H}}/\text{Hz}$
1	68.67	5.65	d	4.75
2	77.18	4.73	dd	2.25; 4.70
3	71.35	5.44	t	2.45
4	77.87	5.00	dd	2.78; 8.67
5	68.93	4.13	dd	2.70; 8.70
6	68.71	3.84	d	12.20
		4.63	dd	3.18; 12.33
C=O (A)	164.40	-	-	-
A-1	116.90	-	-	-
A-2	116.08	-	-	-
A-3	146.89	-	-	-
A-4	138.57	-	-	-
A-5	144.20	-	-	-
A-6	121.61	-	-	-
C=O (B)	170.83	6.43	s	-
B-1	116.78	-	-	-
B-2	107.36	-	-	-
B-3	146.22	-	-	-
B-4	135.24	-	-	-
B-5	144.54 <sup>a</sup>	-	-	-
B-6	126.17	-	-	-
C=O (C)	169.10	6.66	s	-
C-1	116.37	-	-	-
C-2	108.59	-	-	-
C-3	145.70	-	-	-
C-4	137.00	-	-	-
C-5	144.95 <sup>a</sup>	-	-	-
C-6	128.19 <sup>b</sup>	-	-	-
C=O (D)	169.70	6.52	s	-
D-1	115.67	-	-	-
D-2	105.60	-	-	-
D-3	145.55	-	-	-
D-4	136.11	-	-	-
D-5	145.18 <sup>a</sup>	-	-	-



D-6	128.37 <sup>b</sup>	-	-	-
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<sup>a</sup>&<sup>b</sup> Assignations may be interchangeable and cannot be verified without further measurements.



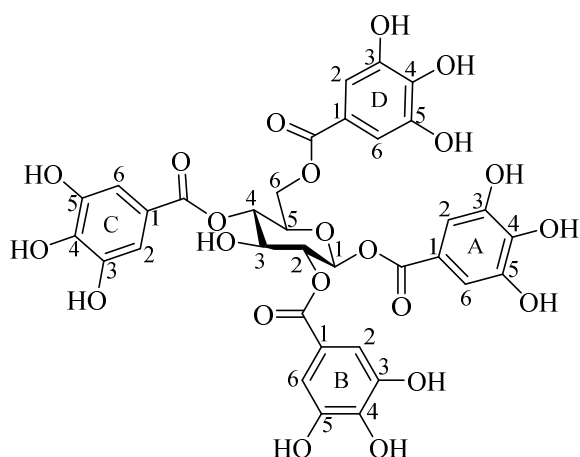
**Figure S5.** Chemical structure of 1,2,3,6-tetra-*O*-galloyl- $\beta$ -*D*-glucose with numbering and definition of rings.

**Table S6.** NMR chemical shifts and coupling constants for 1,2,3,6-tetra-*O*-galloyl- $\beta$ -*D*-glucose. Measured with Bruker Avance-III 600 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Haddock et al. [5].

Position	$\delta$ <sup>13</sup> C/ppm	$\delta$ <sup>1</sup> H/ppm	multiplicity	J <sub>H,H</sub> /Hz
1	93.57	6.18	d	8.35
2	71.87	5.47	dd	8.35; 9.90
3	75.98	5.67	dd	8.90; 9.80
4	69.42	4.11	m	-
5	76.14	4.13	m	-
6	63.73	4.59	m	-
C=O (A)	165.09	-	-	-
A-2	110.09/110/166/110.26/110/39 <sup>a</sup>	7.09	s	-
A-6	110.09/110/166/110.26/110/39 <sup>a</sup>	7.09	s	-
C=O (B)	165.84	-	-	-
B-2	110.09/110/166/110.26/110/39 <sup>a</sup>	7.00	s	-
B-6	110.09/110/166/110.26/110/39 <sup>a</sup>	7.00	s	-
C=O (C)	166.25	-	s-	-
C-2	110.09/110/166/110.26/110/39 <sup>a</sup>	7.07	s	-
C-6	110.09/110/166/110.26/110/39 <sup>a</sup>	7.07	s	-
C=O (D)	166.68	-	-	-
D-2	110.09/110/166/110.26/110/39 <sup>a</sup>	7.18	s	-
D-6	110.09/110/166/110.26/110/39 <sup>a</sup>	7.18	s	-

\*Complete <sup>13</sup>C assignation could not be made due to low amount of analyte available.

<sup>a</sup> Assignations may be interchangeable and cannot be verified without further measurements.



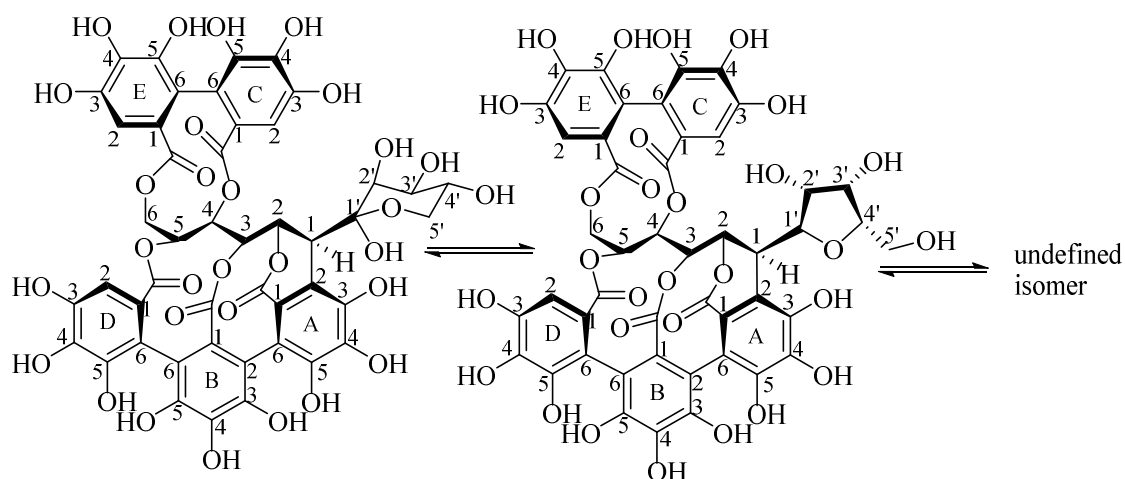
**Figure S6.** Chemical structure of 1,2,4,6-tetra-*O*-galloyl- $\beta$ -*D*-glucose with numbering and definition of rings.

**Table S7.** NMR chemical shifts and coupling constants for 1,2,4,6-tetra-*O*-galloyl- $\beta$ -*D*-glucose. Measured with Bruker Avance-III 600 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Haddock et al. [5].

Position	$\delta$ <sup>13</sup> C/ppm	$\delta$ <sup>1</sup> H/ppm	multiplicity	J <sub>H,H</sub> /Hz
1	93.51	6.11	d	8.45
2	71.75	5.41	t	9.50
3	74.14	4.31	m	-
4	73.94	5.40	dd	8.50; 9.50
5	73.45	4.39	td	5.54; 14.06
6	63.25	4.27	dd	4.83; 12.03
		4.50	dd	1.44; 11.94
C=O (A)	165.17	-	-	-
A-2	110.09/110/166/110.26/110/39 <sup>a</sup>	7.09	s	-
A-6	110.09/110/166/110.26/110/39 <sup>a</sup>	7.09	s	-
C=O (B)	165.94	-	-	-
B-2	110.09/110/166/110.26/110/39 <sup>a</sup>	7.11	s	-
B-6	110.09/110/166/110.26/110/39 <sup>a</sup>	7.11	s	-
C=O (C)	165.94	-	-	-
C-2	110.09/110/166/110.26/110/39 <sup>a</sup>	7.17	s	-
C-6	110.09/110/166/110.26/110/39 <sup>a</sup>	7.17	s	-
C=O (D)	166.53	-	-	-
D-2	110.09/110/166/110.26/110/39 <sup>a</sup>	7.16	s	-
D-6	110.09/110/166/110.26/110/39 <sup>a</sup>	7.16	s	-

\*Complete <sup>13</sup>C assignation could not be made due to low amount of analyte available.

<sup>a</sup> Assignations may be interchangeable and cannot be verified without further measurements.



**Figure S7.** Chemical structure of grandinin with numbering and definition of rings.

**Table S8.** NMR chemical shifts and coupling constants for the main isomer of grandinin (40.7 %). Measured with Bruker Avance-III 500 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Hervé du Penhoat et al. [6].

Position	$\delta^{13}\text{C}/\text{ppm}$	$\delta^1\text{H}/\text{ppm}$	multiplicity	$J_{\text{H,H}}/\text{Hz}$
1	46.81	3.55	brs	-
2	72.29	5.52	brs	-
3	71.84	4.55	brd	6.80
4	70.10	5.26	t	6.98
5	71.38	5.65	brd	7.05
6	65.67	3.99	d	12.21
		5.02	dd	2.30; 12.90
2'	-	4.42	d	3.00
3'	-	4.12	td	3.37; 9.30
4'	-	4.08	m	-
		3.81	d	10.65
5'	-	3.86	dd	5.60; 10.85
C=O (A)	164.16	-	-	-
C=O (B)	165.39/165.49 <sup>a</sup>	-	-	-
C=O (C)	166.64/166.62/166.64 <sup>b</sup>	-	-	-
C-2	110.62	7.47	s	-
C=O (D)	166.47/166.53/166.55 <sup>c</sup>	-	-	-
D-2	109.14/109.18/109.23 <sup>d</sup>	6.75	s	-
C=O (E)	169.07	-	-	-
E-2	107.58	6.58	s	-

\* Grandinin occurs as three isomers in solution with the percentage ratios between the isomers being (40.7 %; 34.1 %; 25.2 %). Most probable explanations for two of the isomers are from the pyranose and furanose forms of lyxose but configuration of the last isomer could not be determined. Distinction between which assigned isomer is which could not be made. Complete <sup>13</sup>C assignment could not be made.

<sup>a-d</sup> Assignations could not be separated between the isomers.

**Table S9.** NMR chemical shifts and coupling constants for the second isomer of grandinins (34.1 %). Measured with Bruker Avance-III 500 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Hervé du Penhoat et al. [6].

Position	$\delta^{13}\text{C}/\text{ppm}$	$\delta^1\text{H}/\text{ppm}$	multiplicity	$J_{\text{H,H}}/\text{Hz}$
1	48.81	3.33	brs	-
2	72.48	5.68	brs	-

Position	$\delta^{13}\text{C}/\text{ppm}$	$\delta^1\text{H}/\text{ppm}$	multiplicity	$J_{\text{H,H}}/\text{Hz}$
3	71.31	4.64	brd	7.10
4	69.81	5.17	t	7.48
5	71.01	5.61	brd	7.75
6	65.67	3.98	d	12.51
		5.08	dd	2.55; 12.95
2'	-	4.24	d	4.65
3'	-	4.40	t	4.13
4'	-	4.06	d	4.50
5'	-	3.91	d	5.31
		3.91	d	6.22
C=O (A)	164.17	-	-	-
C=O (B)	165.49	-	-	-
C=O (C)	166.64/166.62/166.64 <sup>a</sup>	-	-	-
C-2	109.14/109.18/109.23 <sup>b</sup>	7.00	-	-
C=O (D)	166.47/166.53/166.55 <sup>c</sup>	-	-	-
D-2	109.14/109.18/109.23 <sup>d</sup>	6.76	-	-
C=O (E)	168.91/168.92 <sup>e</sup>	-	-	-
E-2	107.87	6.62	-	-

\* Complete  $^{13}\text{C}$  assignment could not be made.

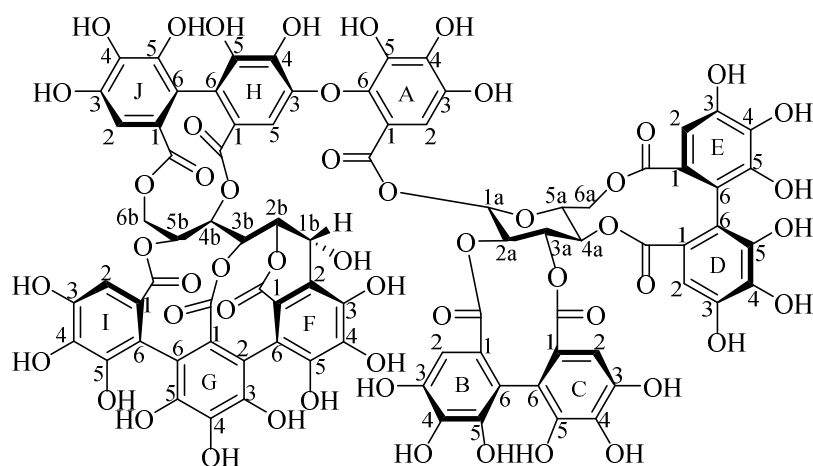
<sup>a-e</sup> Assignations could not be separated between the isomers.

**Table S10.** NMR chemical shifts and coupling constants for the third isomer of grandinin (25.2 %). Measured with Bruker Avance-III 500 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Hervé du Penhoat et al. [6].

Position	$\delta^{13}\text{C}/\text{ppm}$	$\delta^1\text{H}/\text{ppm}$	multiplicity	$J_{\text{H,H}}/\text{Hz}$
1	48.68	3.37	brs	-
2	71.66	5.70	brs	-
3	71.18	4.51	brd	6.80
4	69.86	5.19	t	7.38
5	71.01	5.61	brd	7.85
6	65.67	3.98	d	12.51
		5.12	dd	2.70; 13.05
2'	-	4.33	d	2.90
3'	-	4.29	t	3.03
4'	-	4.01	d	3.59
5'	-	3.74	d	12.90
		4.25	d	12.66
C=O (A)	164.41	-	-	-
C=O (B)	165.39/165.49 <sup>a</sup>	-	-	-
C=O (C)	166.64/166.62/166.64 <sup>b</sup>	-	-	-
C-2	109.2280	7.14	s	-
C=O (D)	166.47/166.53/166.55 <sup>c</sup>	-	-	-
D-2	109.14/109.18/109.23 <sup>d</sup>	6.76	s	-
C=O (E)	168.91/168.92 <sup>e</sup>	-	-	-
E-2	107.92	6.63	s	-

\* Complete  $^{13}\text{C}$  assignment could not be made.

<sup>a-e</sup> Assignations could not be separated between the isomers.

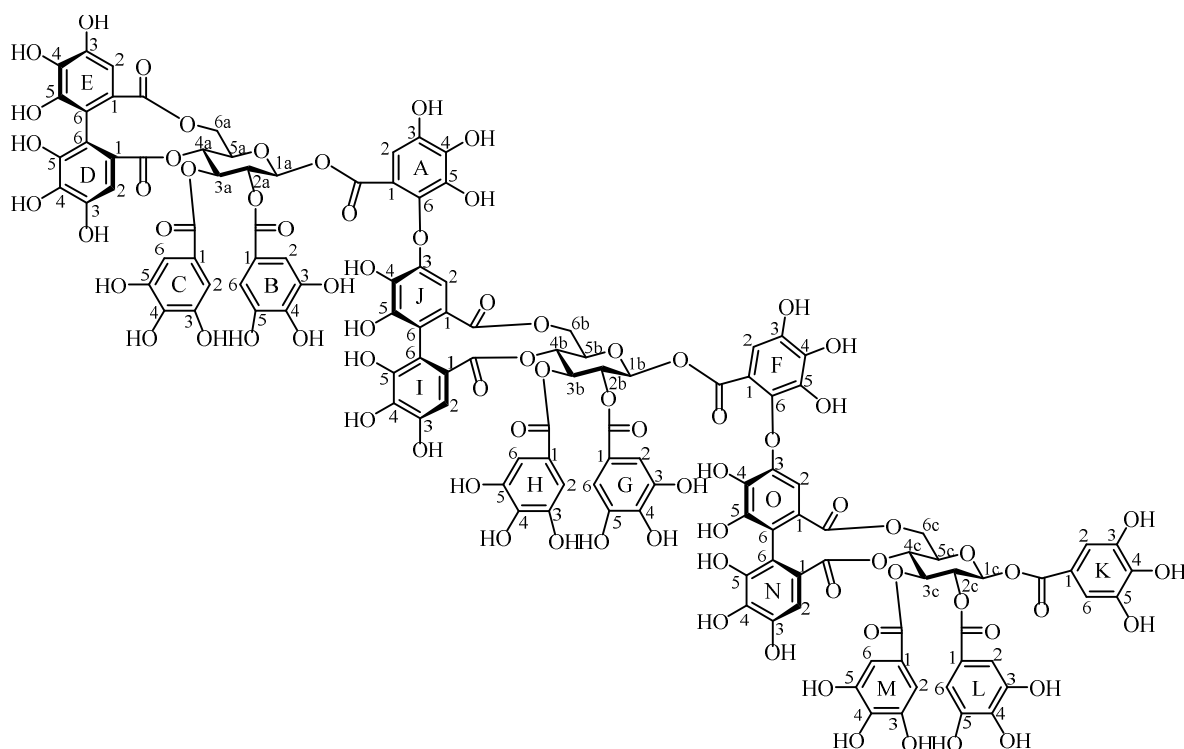


**Figure S8.** Chemical structure of cocciferin D<sub>2</sub> with with numbering and definition of rings.

**Table S11.** NMR chemical shifts and coupling constants for cocciferin D<sub>2</sub>. Measured with Bruker Avance-III 600 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Ito et al. [7].

Position	$\delta$ <sup>13</sup> C/ppm	$\delta$ <sup>1</sup> H/ppm	multiplicity	$J_{H,H}$ /Hz
1a	92.72	6.15	d	8.55
2a	76.47	5.14	t	10.07
3a	77.78	5.38	dd	9.40; 10.20
4a	69.46 <sup>a</sup>	5.13	t	8.85
5a	73.96	4.43	ddd	0.89; 6.94; 9.79
6a	63.52	3.86	brd	12.75
		5.31	dd	6.80; 13.30
C=O (A)	163.90	-	--	-
A-2	110.46	7.27	s	-
C=O (B)	166.39	-	-	-
B-2	106.40	6.49	s	-
C=O (C)	169.68	-	-	-
C-2	107.85	6.35	s	-
C=O (D)	168.35	-	-	-
D-2	109.02	6.68	s	-
C=O (E)	168.29	-	-	-
E-2	108.10	6.51	s	-
1b	67.98	5.41	d	4.90
2b	74.11	4.77	dd	1.18; 4.88
3b	66.79	4.91	dd	1.05; 6.85
4b	69.53 <sup>a</sup>	5.12	t	7.32
5b	71.85	5.55	dd	2.18; 7.38
6b	65.78	3.98	d	12.85
		5.14	brd	-
C=O (F)	163.95	-	-	-
C=O (G)	165.95	-	-	-
C=O (H)	169.57	-	-	-
H-2	108.18	6.41	s	-
C=O (I)	167.00	-	-	-
I-2	109.59	6.78	s	-
C=O (J)	169.31	-	-	-
J-2	108.31	6.59	s	-

<sup>a</sup>Complete <sup>13</sup>C assignation could not be made.



**Figure S9.** Chemical structure of rugosin G with numbering and definition of rings.

**Table S12.** NMR chemical shifts and coupling constants for rugosin G. Measured with Bruker Avance-III 600 spectrometer at 25 °C in acetone-*d*<sub>6</sub>. Assignations match those found in Ito et al. [8].

Position	$\delta^{13}\text{C}/\text{ppm}$	$\delta^1\text{H}/\text{ppm}$	multiplicity	$J_{\text{H,H}}/\text{Hz}$
1a	93.500/93.715/94.140 <sup>a</sup>	6.09	d	8.34
2a	72.081/72.132 <sup>b</sup>	5.53	dd	8.49; 9.45
3a	73.642/73.699 <sup>c</sup>	5.78	t	9.75
4a	71.105/71.140/71.166 <sup>d</sup>	5.09	t	9.96
5a	73.321/73.414/73.473 <sup>e</sup>	4.43	dd	6.78; 10.02
6a	63.435 <sup>f</sup>	3.71	d	13.32
C=O (A)	162.618	-	-	-
A-2	110.508-110.905 <sup>g</sup>	7.153	s	-
C=O (B)	166.027/166.040/166.070 <sup>h</sup>	-	-	-
B-2	110.508-110.905 <sup>g</sup>	7.002/7.018/7.026 <sup>n</sup>	s	-
B-6	110.508-110.905 <sup>g</sup>	7.002/7.018/7.026 <sup>n</sup>	s	-
C=O (C)	166.651/166.677 <sup>i</sup>	-	-	-
C-2	110.508-110.905 <sup>g</sup>	6.974/6.994/7.006 <sup>o</sup>	s	-
C-6	110.508-110.905 <sup>g</sup>	6.974/6.994/7.006 <sup>o</sup>	s	-
C=O (D)	168.112 <sup>j</sup>	-	-	-
D-2	108.126/108.240 <sup>k</sup>	6.462	s	-
C=O (E)	168.2242 <sup>l</sup>	-	-	-
E-2	105.623 <sup>m</sup>	6.220 <sup>c</sup>	s	-
1b	93.500/93.715/94.140 <sup>a</sup>	6.12	d	8.28
2b	72.081/72.132 <sup>b</sup>	5.53	dd	8.49; 9.45
3b	73.642/73.699 <sup>c</sup>	5.78	t	9.75
4b	71.105/71.140/71.166 <sup>d</sup>	5.16	t	10.01
5b	73.321/73.414/73.473 <sup>e</sup>	4.47	dd	6.99; 9.69
6b	63.435 <sup>f</sup>	3.81	d	13.32

		5.31	dd	6.48; 13.44
C=O (F)	162.920	-	-	-
A-2	110.508-110.905 <sup>s</sup>	7.128	s	-
C=O (G)	166.027/166.040/166.070 <sup>h</sup>	-	-	-
B-2	110.508-110.905 <sup>s</sup>	7.002/7.018/7.026 <sup>n</sup>	s	-
B-6	110.508-110.905 <sup>s</sup>	7.002/7.018/7.026 <sup>n</sup>	s	-
C=O (H)	166.651/166.677 <sup>i</sup>	-	-	-
C-2	110.508-110.905 <sup>s</sup>	6.974/6.994/7.006 <sup>o</sup>	s	-
C-6	110.508-110.905 <sup>s</sup>	6.974/6.994/7.006 <sup>o</sup>	s	-
C=O (I)	168.018	-	-	-
C-2	108.126/108.240 <sup>k</sup>	6.458	s	-
C=O (J)	168.396	-	-	-
C-2	108.708	6.674	s	-
1c	93.500/93.715/94.140 <sup>a</sup>	6.19	d	8.34
2c	72.081/72.132 <sup>b</sup>	5.61	dd	8.43; 8.51
3c	73.642/73.699 <sup>c</sup>	5.84	t	9.75
4c	71.105/71.140/71.166 <sup>d</sup>	5.15	t	9.93
5c	73.321/73.414/73.473 <sup>e</sup>	4.53	dd	6.57; 10.05
6c	63.435 <sup>f</sup>	3.78	d	13.32
		5.28	dd	6.60; 13.68
C=O (K)	165.519	-	-	-
A-2	110.508-110.905 <sup>s</sup>	7.150	s	-
A-6	110.508-110.905 <sup>s</sup>	7.150	s	-
C=O (L)	166.027/166.040/166.070 <sup>h</sup>	-	-	-
B-2	110.508-110.905 <sup>s</sup>	7.002/7.018/7.026 <sup>n</sup>	s	-
B-6	110.508-110.905 <sup>s</sup>	7.002/7.018/7.026 <sup>n</sup>	s	-
C=O (M)	166.651/166.677 <sup>i</sup>	-	-	-
C-2	110.508-110.905 <sup>s</sup>	6.974/6.994/7.006 <sup>o</sup>	s	-
C-6	110.508-110.905 <sup>s</sup>	6.974/6.994/7.006 <sup>o</sup>	s	-
C=O (N)	168.112 <sup>j</sup>	-	-	-
C-2	108.126/108.240 <sup>k</sup>	6.474	s	-
C=O (O)	168.2242 <sup>l</sup>	-	-	-
C-2	105.623 <sup>m</sup>	6.232 <sup>c</sup>	s	-

\*Complete <sup>13</sup>C assignment could not be made due to the complexity of the structure.

<sup>a-o</sup> Assignations may be interchangeable and cannot be verified without further measurements.

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