

2D NMR Barcoding and Differential Analysis of Complex Mixtures for Chemical Identification: the *Actaea* Triterpenes

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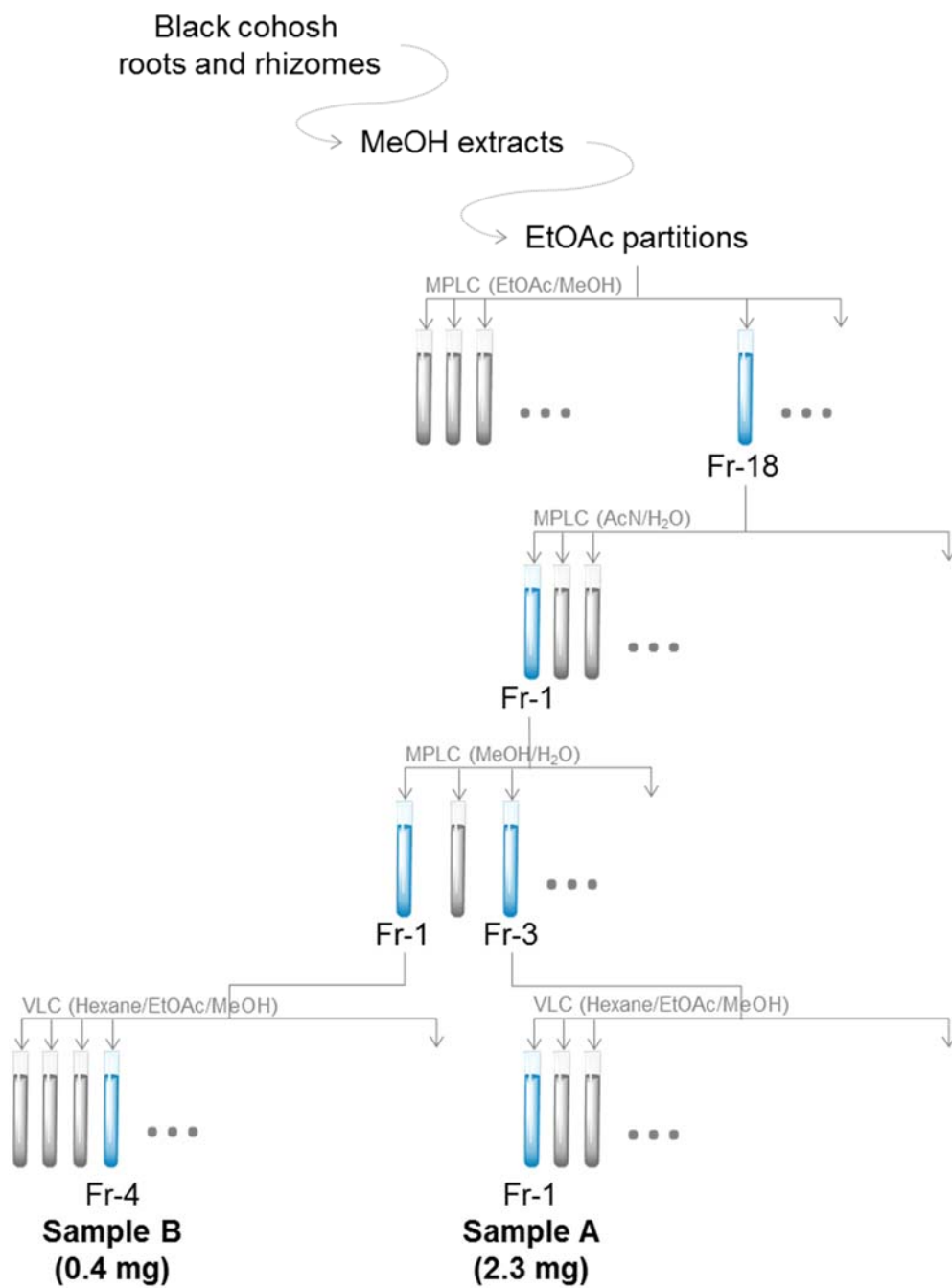
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■ SUPPORTING INFORMATION

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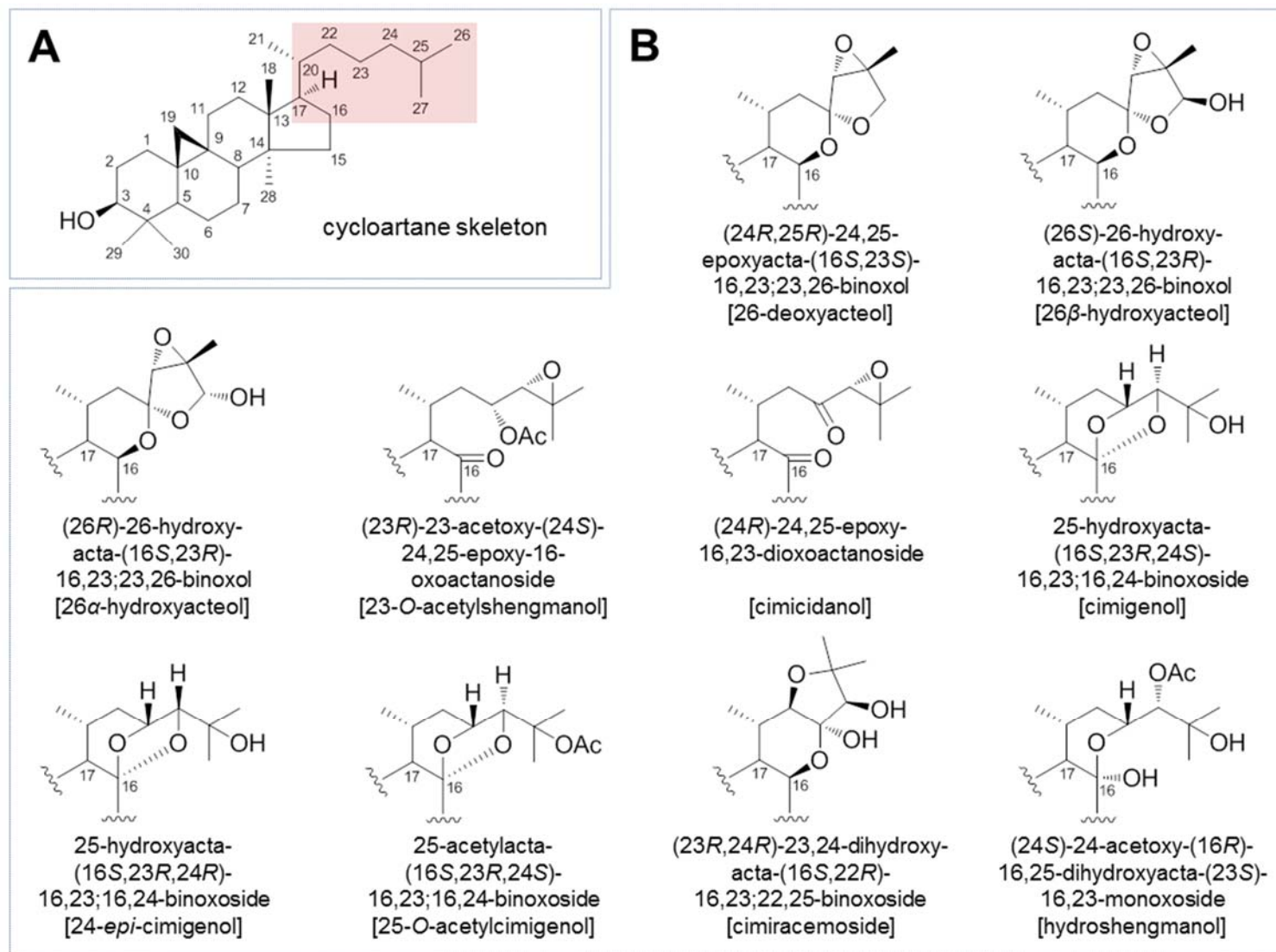
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S1: The Fractionation Procedure for the Preparation of Triterpene-enriched Samples

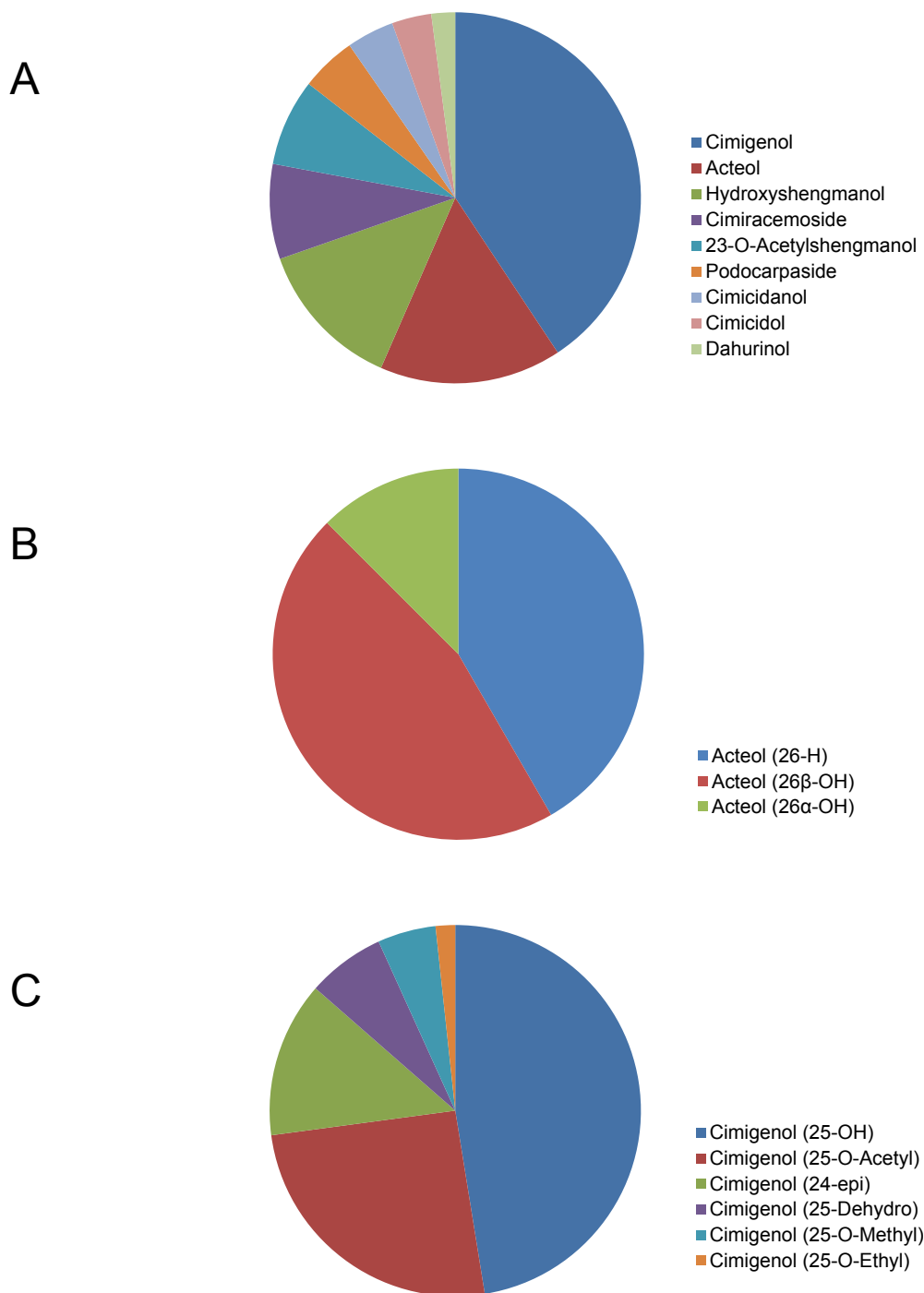


S2: Structures and Newly Established Nomenclature of the *Actaea* Triterpenes Used as Model Compounds in This Study.

(A) The *Actaea* triterpenes derive from the same cycloartane skeleton, consisting of a pentacyclic core and a side chain attached to C-17. (B) The structural diversity of these triterpenes results from several variants of their side chains which are often biosynthetically cyclized onto C-16. Each depicted subtype is accompanied by the name according to the newly established nomenclature (Qiu et al. J. Nat. Prod. 2012, 75, 432 [ref.¹⁴] in main text). Compared to the common names, which are given in squared brackets, the new systematic names more clearly differentiate the key structural features which also relate to the HMBC barcodes used in the present study.



S3: The Distribution of Structural Types of *Actaea* Triterpenes in the In-house Database



S4: The NMR Data of *Actaea* Triterpenes in the In-house Database

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
23- <i>O</i> -acetylshengmanol-3- <i>O</i> - α -L-arabinopyranoside	<i>racemosa</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	500	1.25	1.40	65.2	58.5	16
cimiracemoside L	<i>racemosa</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	300	1.26	1.40	65.2	58.6	3
23- <i>O</i> -acetyl-1 α -hydroxyshengmanol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	500	1.24	1.37	65.0	58.4	25
7 β -hydroxy-23- <i>O</i> -acetylshengmanol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	n/a	1.23	1.38	65.0	58.4	28
cimiracemoside M	<i>racemosa</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	300	1.26	1.41	65.2	58.6	3
23- <i>O</i> -acetylshengmanol-3- <i>O</i> - β -D-glucopyranosyl-(1 \rightarrow 3)- β -D-xylopyranoside	<i>simplex</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	n/a	1.29	1.44	64.8	58.4	27
23- <i>O</i> -acetylshengmanol-3- <i>O</i> -(2'- <i>O</i> -malonyl)- β -D-xylopyranoside	<i>simplex</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	500	1.27	1.41	65.1	58.6	30
23- <i>O</i> -acetyl-7,8-didehydroshengmanol-3- <i>O</i> - α -L-arabinopyranoside	<i>simplex</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	400	1.30	1.42	65.3	58.5	19
23- <i>O</i> -acetyl-7,8-didehydroshengmanol-3- <i>O</i> - β -D-galactopyranoside	<i>simplex</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	500	1.29	1.43	65.2	58.6	29
23- <i>O</i> -acetyl-7,8-dehydroshengmanol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	500	1.30	1.43	65.1	58.5	30

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
23- <i>O</i> -acetyl-7,8-dehydroshengmanol-3- <i>O</i> -(2'- <i>O</i> -malonyl)- β -D-xylopyranoside	<i>simplex</i>	23- <i>O</i> -Acetylshengmanol	Pyridine- <i>d</i> ₅	500	1.28	1.42	65.2	58.6	30
26-deoxycimicifugoside	<i>simplex</i>	Acteol	Pyridine- <i>d</i> ₅	400	--	1.47	62.4	62.4	29
26-deoxyactein	<i>n/a</i>	Acteol	Pyridine- <i>d</i> ₅	270 or 400	--	1.41	63.3	63.3	9, 10
2'- <i>O</i> -acetyl-26-deoxyactein	<i>foetida</i>	Acteol	Pyridine- <i>d</i> ₅	400	--	1.50	62.5	62.7	13
cimifoside D	<i>foetida</i>	Acteol	Pyridine- <i>d</i> ₅	500	--	1.54	62.5	62.2	40
cimiracemoside I	<i>racemosa</i>	Acteol (23- <i>epi</i>)	Pyridine- <i>d</i> ₅	900	--	1.47	62.6	62.1	1, 3
cimiracemoside N	<i>racemosa</i>	Acteol (23- <i>epi</i>)	Pyridine- <i>d</i> ₅	300	--	1.48	62.5	62.2	3
23- <i>epi</i> -26-deoxyactein	<i>racemosa</i>	Acteol (23- <i>epi</i>)	Pyridine- <i>d</i> ₅	500	--	1.45	62.5	62.3	10
12-deacetoxy-15 α -hydroxy-23- <i>epi</i> -26-deoxyactein	<i>vaginata</i>	Acteol (23- <i>epi</i>)	Pyridine- <i>d</i> ₅	500	--	1.41	62.4	62.1	46
12-deacetoxy-23- <i>epi</i> -26-deoxyactein	<i>vaginata</i>	Acteol (23- <i>epi</i>)	Pyridine- <i>d</i> ₅	500	--	1.43	62.5	62.1	46
4'- <i>O</i> -acetyl-23- <i>epi</i> -26-deoxycimifugoside	<i>asiatica</i>	Acteol (23- <i>epi</i>)	Pyridine- <i>d</i> ₅	300	--	1.48	62.7	62.9	36

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
cimiracemoside P	<i>racemosa</i>	Acteol (26=O)	Pyridine- <i>d</i> ₅	300	--	1.65	62.7	58.6	3
acetylacteol-3- <i>O</i> -arabinoside (26 <i>S</i>)	<i>heracleifolia</i>	Acteol (26β-OH)	DMSO- <i>d</i> ₆	400	--	1.43	61.9	64.5	26
(26 <i>S</i>)-bugbanoside B	<i>simplex</i>	Acteol (26β-OH)	Pyridine- <i>d</i> ₅	400	--	1.75	63.6	65.5	43
(26 <i>R</i>)-bugbanoside B	<i>simplex</i>	Acteol (26α-OH)	Pyridine- <i>d</i> ₅	400	--	1.59	63.8	63.9	43
actein (26 <i>S</i>)	<i>n/a</i>	Acteol (26β-OH)	Pyridine- <i>d</i> ₅	n/a	--	1.78	63.5	65.5	47
actein (26 <i>R</i>)	<i>n/a</i>	Acteol (26α-OH)	Pyridine- <i>d</i> ₅	270 or 400	--	1.63	62.9	63.9	47
2'- <i>O</i> -acetylactein	<i>foetida</i>	Acteol (26β-OH)	Pyridine- <i>d</i> ₅	400	--	1.88	63.7	65.9	13
cimifoside E (26 <i>S</i>)	<i>foetida</i>	Acteol (26β-OH)	Pyridine- <i>d</i> ₅	400 or 500	--	1.74	63.5	65.6	42
cimiracemoside O (26 <i>S</i>)	<i>racemosa</i>	Acteol (26β-OH)	Pyridine- <i>d</i> ₅	300	--	1.79	63.4	65.8	3
(26 <i>S</i>)-bugbanoside A	<i>simplex</i>	Acteol (26β-OH)	Pyridine- <i>d</i> ₅	400	--	1.75	63.6	65.5	43
(26 <i>R</i>)-bugbanoside A	<i>simplex</i>	Acteol (26α-OH)	Pyridine- <i>d</i> ₅	400	--	1.60	63.0	63.9	43

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
cimifugoside (265)	<i>simplex</i>	Acteol (26 β -OH)	Pyridine- <i>d</i> ₅	500	--	1.78	63.4	65.6	47
2'- <i>O</i> -malonylcimicifugoside (265)	<i>simplex</i>	Acteol (26 β -OH)	Pyridine- <i>d</i> ₅	500	--	1.79	63.4	65.6	30
3'- <i>O</i> -acetylcimicifugoside (265)	<i>asiatica</i>	Acteol (26 β -OH)	Pyridine- <i>d</i> ₅	300	--	1.81	63.8	66.1	36
cimicidanol	<i>heracleifolia</i>	Cimicidanol	Pyridine- <i>d</i> ₅	400	1.37	1.35	65.7	60.6	26
bugbanoside D	<i>simplex</i>	Cimicidanol	Pyridine- <i>d</i> ₅	500	1.30	1.35	65.6	60.9	34
cimicidanol-3- <i>O</i> -arabinoside	<i>heracleifolia</i>	Cimicidanol	Pyridine- <i>d</i> ₅	400	1.31	1.37	65.5	60.5	26
bugbanoside E	<i>simplex</i>	Cimicidanol	Pyridine- <i>d</i> ₅	500	1.30	1.36	65.7	61.0	34
cimicifugoside H5	<i>n/a</i>	Cimicidanol	Pyridine- <i>d</i> ₅	270 or 400	1.31	1.36	65.8	60.7	9
cimicifol	<i>heracleifolia</i>	Cimicidanol	Pyridine- <i>d</i> ₅	400	1.29	1.33	65.6	60.3	26
bugbanoside C	<i>simplex</i>	Cimicidol	Pyridine- <i>d</i> ₅	500	1.52	1.54	83.7	72.3	34
cimicidol-3- <i>O</i> - β -xyloside	<i>heracleifolia</i>	Cimicidol	Pyridine- <i>d</i> ₅	400	1.54	1.66	84.0	72.5	26

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
cimicifugoside H1	<i>n/a</i>	Cimicidol	Pyridine- <i>d</i> ₅	270 or 400	1.35	1.36	65.8	60.7	9
cimicifugoside H2	<i>n/a</i>	Cimicidol	Pyridine- <i>d</i> ₅	270 or 400	1.55	1.67	84.0	72.5	9
15 α -hydroxycimicidol-3- <i>O</i> - β -xyloside	<i>heracleifolia</i>	Cimicidol	Pyridine- <i>d</i> ₅	400	1.50	1.63	83.9	72.4	26
25-chlorodeoxycimigenol	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	900	1.70	1.71	89.4	71.6	39
cimigenol-15- <i>O</i> - β -D-glucopyranoside	<i>dahurica</i>	Cimigenol	Pyridine- <i>d</i> ₅	400	1.23	1.40	89.8	71.0	14
7,8-didehydrocimigenol	<i>heracleifolia</i>	Cimigenol	Chloroform- <i>d</i> ₃	400	1.20	1.20	88.8	71.8	8
cimiracemoside A	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.50	1.50	90.3	71.3	4
12 β ,21-dihydroxycimigenol-3- <i>O</i> - α -L-arabinopyranoside	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.49	1.49	88.8	70.9	16
cimiracemoside B	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.46	1.48	90.0	71.1	4
1 α -hydroxycimigenol-3- <i>O</i> - α -L-arabinopyranoside	<i>simplex</i>	Cimigenol	Pyridine- <i>d</i> ₅	400	1.45	1.48	90.3	71.9	29
cimiracemoside C	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.47	1.49	90.4	71.2	4

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
cimiracemoside D	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.47	1.49	90.0	71.0	4
12 β -hydroxycimigenol-3- <i>O</i> - β -D-arabinopyranoside	<i>simplex</i>	Cimigenol	Pyridine- <i>d</i> ₅	300	1.51	1.55	89.7	70.8	22
cimicifoetoside A	<i>foetida</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.44	1.47	90.2	71.0	41
cimigenol 3- <i>O</i> - β -D-galactopyranoside	<i>simplex</i>	Cimigenol	Pyridine- <i>d</i> ₅	400	1.46	1.48	88.7	71.0	19
1 α -hydroxycimigenol-3- <i>O</i> - β -D-galactopyranoside	<i>simplex</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.47	1.50	89.9	70.8	29
(23 <i>R</i> ,24 <i>S</i>)-16 β ,23;16 α ,24-diepoxy-cycloartane-3 β ,12 β ,25-triol-3- <i>O</i> - β -D-xylopyranoside	<i>n/a</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.47	1.54	90.3	71.2	15
1 α -hydroxycimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	300	1.47	1.50	90.2	71.1	25
cimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	600	1.50	1.55	90.2	71.2	12
(23 <i>R</i> ,24 <i>R</i>)-16 β ,23;16 α ,24-diepoxy-12 β -acetoxy-cycloart-3 β ,15 α ,25-triol-3- <i>O</i> - β -D-xylopyranoside	<i>n/a</i>	Cimigenol	Pyridine- <i>d</i> ₅	500	1.27	1.44	84.1	68.6	15
cimigenol-3- <i>O</i> - β -D-xyloside	<i>racemosa</i>	Cimigenol	Pyridine- <i>d</i> ₅	900	1.48	1.50	90.2	71.0	39
12 β -hydroxycimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	Cimigenol	Pyridine- <i>d</i> ₅	300	1.49	1.52	90.2	71.3	22

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
7 β -hydroxycimigenol-3-O- β -D-xylopyranoside	<i>simplex</i>	Cimigenol	Pyridine- d_5	300	1.49	1.52	90.3	71.2	22
3'-O-acetyl-cimigenol-3-O- β -D-xylopyranoside	<i>acerina</i>	Cimigenol	Pyridine- d_5	400	1.46	1.49	90.1	70.9	32
(3',12 β)-O-diacetylcimigenol-3-O- β -D-xylopyranoside	<i>asiatica</i>	Cimigenol	Pyridine- d_5	300	1.50	1.51	90.3	71.6	36
cimifoside A	<i>foetida</i>	Cimigenol	Pyridine- d_5	500	1.49	1.50	90.1	71.0	40
12 β -hydroxycimigenol-3-O- β -D-xylopyranoside-(1 \rightarrow 3)- β -D-xylopyranoside	<i>vaginata</i>	Cimigenol	Pyridine- d_5	500	1.48	1.49	90.0	71.0	46
7,8-didehydrocimigenol-3-O- α -L-arabinopyranoside	<i>simplex</i>	Cimigenol	Pyridine- d_5	400	1.47	1.49	90.3	72.1	29
bugbanoside F	<i>simplex</i>	Cimigenol	Pyridine- d_5	500	1.51	1.55	90.0	71.2	34
7,8-didehydrocimigenol-3-O- β -D-galactopyranoside	<i>simplex</i>	Cimigenol	Pyridine- d_5	400	1.46	1.49	90.3	71.0	19
(23R,24S)-16 β ,23;16 α ,24-diepoxyart-7-en-3 β ,11 β ,25-triol-3-O- β -D-xylopyranoside	<i>n/a</i>	Cimigenol	Pyridine- d_5	500	1.46	1.52	90.6	71.0	15
24- <i>epi</i> -7,8-didehydrocimigenol	<i>heracleifolia</i>	Cimigenol (24- <i>epi</i>)	Chloroform- d_3	400	1.33	1.22	83.3	68.7	8
3-keto-24- <i>epi</i> -7,8-didehydrocimigenol	<i>heracleifolia</i>	Cimigenol (24- <i>epi</i>)	Pyridine- d_5	400	1.43	1.29	83.3	68.7	8

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
(23 <i>R</i> ,24 <i>R</i>)-16 β ,23;16 α ,24-diepoxy-cycloart-7-en-3 β ,12 β ,15 α ,25-tetraol-3- <i>O</i> - β -D-xylopyranoside	<i>n/a</i>	Cimigenol (24- <i>epi</i>)	Pyridine- <i>d</i> ₅	500	1.34	1.45	84.1	68.7	15
(23 <i>R</i> ,24 <i>R</i>)-16 β ,23;16 α ,24-diepoxy-12 β -acetoxy-cycloart-7-en-3 β ,15 α ,25-triol-3- <i>O</i> - β -D-xylopyranoside	<i>n/a</i>	Cimigenol (24- <i>epi</i>)	Pyridine- <i>d</i> ₅	500	1.32	1.44	84.1	68.6	15
24- <i>epi</i> -cimigenol-3- <i>O</i> - α -L-arabinopyranoside		Cimigenol (24- <i>epi</i>)	Pyridine- <i>d</i> ₅		1.26	1.42	84.1	68.6	48
24- <i>epi</i> -7,8-didehydrocimigenol-3-xyloside	<i>heracleifolia</i>	Cimigenol (24- <i>epi</i>)	Pyridine- <i>d</i> ₅	400	1.31	1.41	84.0	68.6	8
2',4'-di- <i>O</i> -acetyl-24- <i>epi</i> -7,8-didehydrocimigenol-3- <i>O</i> -xyloside	<i>heracleifolia</i>	Cimigenol (24- <i>epi</i>)	Chloroform- <i>d</i> ₃	400	1.22	1.33	83.3	68.7	8
3'- <i>O</i> -acetyl-24- <i>epi</i> -7,8-didehydrocimigenol-3-xyloside	<i>heracleifolia</i>	Cimigenol (24- <i>epi</i>)	Pyridine- <i>d</i> ₅	400	1.28	1.42	84.0	68.6	8
cimiracemoside J	<i>racemosa</i>	Cimigenol (25-Dehydro)	Pyridine- <i>d</i> ₅	300	--	1.85	86.5	145.8	3
cimiracemoside K	<i>racemosa</i>	Cimigenol (25-Dehydro)	Pyridine- <i>d</i> ₅	300	--	1.85	86.5	145.8	3
25-anhydrocimigenol-3- <i>O</i> -xyloside	<i>heracleifolia</i>	Cimigenol (25-Dehydro)	Pyridine- <i>d</i> ₅	400	--	1.84	86.6	145.8	26
25,26-anhydrocimigenol-3- <i>O</i> - β -D-(2'- <i>O</i> -acetyl)xylopyranoside	<i>vaginata</i>	Cimigenol (25-Dehydro)	Pyridine- <i>d</i> ₅	500	--	1.83	86.7	145.9	46
25- <i>O</i> -acetylcimigenol	<i>heracleifolia</i>	Cimigenol (25- <i>O</i> -Acetyl)	Chloroform- <i>d</i> ₃	400	1.47	1.41	86.4	82.6	8

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
25- <i>O</i> -acetyl-7,8-didehydrocimigenol	<i>heracleifolia</i>	Cimigenol (25- <i>O</i> -Acetyl)	Chloroform- <i>d</i> ₃	400	1.48	1.42	86.3	82.5	8
25- <i>O</i> -acetyl-12 β -hydroxycimigenol-3- <i>O</i> - α -L-arabinoside	<i>racemosa</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	500	1.69	1.71	86.7	83.1	16
25- <i>O</i> -acetylcimigenol-3- <i>O</i> - α -L-arabinopyranoside	<i>dahurica</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	400 or 500	1.64	1.66	86.7	83.1	33
cimicifoetoside B	<i>foetida</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	500	1.65	1.67	86.8	83.2	41
25- <i>O</i> -acetylcimigenol-3- <i>O</i> - β -D-galactopyranoside	<i>simplex</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	400	1.67	1.70	86.5	83.0	19
25- <i>O</i> -acetylcimigenol-3- <i>O</i> - β -D-glucopyranoside	<i>simplex</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	400	1.67	1.70	86.6	83.0	19
25- <i>O</i> -acetyl-7- β -hydroxycimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	300	1.73	1.75	86.6	83.4	22
25- <i>O</i> -acetyl-1 α -hydroxycimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	400	1.66	1.68	86.7	83.2	25
25- <i>O</i> -acetylcimigenol-3- <i>O</i> - β -D-glucopyranosyl-(1 \rightarrow 3)- β -D-xylopyranoside	<i>simplex</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	n/a	1.67	1.71	86.5	82.9	27
(4',25)- <i>O</i> -diacetylcimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>asiatica</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	300	1.70	1.73	87.2	83.6	36
cimifoside B	<i>foetida</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	500	1.44	1.47	86.8	83.2	40

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
25- <i>O</i> -acetylcimigenol-3- <i>O</i> - β -D-(2'- <i>O</i> -acetyl)xylopyranoside	<i>vaginata</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	500	1.65	1.67	86.7	83.1	45
25- <i>O</i> -acetyl-7,8-didehydrocimigenol-3- <i>O</i> - α -L-arabinopyranoside	<i>simplex</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	400	1.68	1.69	86.9	83.4	29
25- <i>O</i> -acetyl-7,8-didehydrocimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	Cimigenol (25- <i>O</i> -Acetyl)	Pyridine- <i>d</i> ₅	400	1.66	1.67	86.8	83.1	29
2'- <i>O</i> -acetyl-25- <i>O</i> -ethylcimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>asiatica</i>	Cimigenol (25- <i>O</i> -Ethyl)	Chloroform- <i>d</i> ₃	300	1.07	1.16	87.9	75.5	36
25- <i>O</i> -methyl-7,8-dehydrocimigenol	<i>simplex</i>	Cimigenol (25- <i>O</i> -Methyl)	Pyridine- <i>d</i> ₅	500	1.28	1.27	88.1	76.3	30
25- <i>O</i> -methylcimigenol-3- <i>O</i> - β -D-galactopyranoside	<i>simplex</i>	Cimigenol (25- <i>O</i> -Methyl)	Pyridine- <i>d</i> ₅	400	1.29	1.39	87.8	78.4	19
2'- <i>O</i> -acetyl-25- <i>O</i> -methylcimigenol-3- <i>O</i> - β -D-xylopyranoside	<i>asiatica</i>	Cimigenol (25- <i>O</i> -Methyl)	Chloroform- <i>d</i> ₃	300	1.07	1.16	87.8	75.8	36
2'- <i>O</i> -malonylcimiaceroside B	<i>simplex</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.76	1.67	83.1	83.7	30
2'- <i>O</i> - β -D-glucopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosylcimiaceroside B	<i>n/a</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.76	1.70	83.3	83.6	11
2'- <i>O</i> -(6'''- <i>O</i> -trans-isoferuloyl)- β -D-glucopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosylcimiaceroside B	<i>n/a</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.77	1.68	83.3	83.6	11
cimiracemoside H	<i>racemosa</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.79	1.72	83.6	83.8	4

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
cimiaceroside B	<i>simplex</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	400	1.75	1.67	83.4	83.6	2
cimiaceroside C	<i>foetida</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.76	1.67	83.3	83.6	40
(20 <i>S</i> ,22 <i>R</i> ,23 <i>S</i> ,24 <i>R</i>)-16 β :23;22:25-diepoxy-3 β ,23,24-trihydroxy-9,19-cycloartane-3- <i>O</i> - β -D-(4'- <i>O</i> -acetyl)xylopyranoside	<i>vaginata</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.76	1.68	83.3	83.6	45
cimiracemoside F	<i>racemosa</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.78	1.70	83.6	84.0	4
cimiracemoside F	<i>racemosa</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.69	1.77	84.4	84.8	5
cimiracemoside G	<i>racemosa</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	500	1.68	1.76	83.3	83.7	4
cimiaceroside A	<i>simplex</i>	Cimiracemoside	Pyridine- <i>d</i> ₅	400	1.67	1.76	83.3	83.6	2
cimiaceroside E	<i>foetida</i>	Cimiracemoside (24-Dehydro)	Pyridine- <i>d</i> ₅	400 or 500	1.51	1.61	30.0	83.4	42
cimiracemoside E	<i>racemosa</i>	Dahurinol	Pyridine- <i>d</i> ₅	500	1.61	1.61	79.9	72.1	4
24- <i>O</i> -acetylisodahuriny-3- <i>O</i> - β -D-(2'- <i>O</i> -acetyl)xylopyranoside	<i>vaginata</i>	Dahurinol	Pyridine- <i>d</i> ₅	500	1.59	1.59	79.8	72.1	45
24- <i>O</i> -acetyldahuriny-3- <i>O</i> - β -D-(2'- <i>O</i> -acetyl)xylopyranoside	<i>vaginata</i>	Dahurinol	Pyridine- <i>d</i> ₅	500	1.48	1.48	80.5	72.0	46

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
23-acetoxy-3,15,24,25-tetrahydroxycycloart-7-en-16-one-3-O- β -D-xylopyranoside	<i>heracleifolia</i>	Hydroxyshengmanol	Pyridine- d_5	500	1.59	1.59	79.5	72.2	44
23,24-diacetoxy-3,15,25-trihydroxycycloart-7-en-16-one-3-O- β -D-xylopyranoside	<i>heracleifolia</i>	Hydroxyshengmanol	Pyridine- d_5	500	1.51	1.52	80.5	71.4	44
24-O-acetyl-25-O-methyl-7,8-dehydroshengmanol	<i>simplex</i>	Hydroxyshengmanol	Pyridine- d_5	500	1.27	1.22	79.3	76.1	30
3-O-arabinosyl-24-O-acetylhydroshengmanol-15-glucoside	<i>dahurica</i>	Hydroxyshengmanol	Pyridine- d_5	270 or 400	1.26	1.38	78.3	72.6	7
24- <i>epi</i> -24-O-acetylhydroshengmanol-3-O- β -D-galactopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- d_5	400	1.45	1.46	81.2	72.8	19
3-O-xylosyl-24-O-acetylhydroshengmanol-15-glucoside	<i>dahurica</i>	Hydroxyshengmanol	Pyridine- d_5	270 or 400	1.28	1.38	78.4	72.6	7
24- <i>epi</i> -7 β -hydroxy-24-O-acetylhydroshengmanol-3-O- β -D-xylopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- d_5	300	1.53	1.57	81.9	72.7	21
25-O-methyl-24-O-acetylhydroshengmanol-3-O- β -D-xylopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- d_5	300	1.25	1.25	79.3	76.0	21
25-O-methyl-7 β -hydroxy-24-O-acetylhydroshengmanol-3-O- β -D-xylopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- d_5	300	1.26	1.28	79.4	76.0	21
25-O-methyl-1 α -hydroxy-24-O-acetylhydroshengmanol-3-O- β -D-xylopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- d_5	300	1.28	1.37	79.3	76.0	21
cimifoside C	<i>foetida</i>	Hydroxyshengmanol	Pyridine- d_5	500	1.63	1.65	82.7	71.2	40

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
24- <i>epi</i> -24- <i>O</i> -acetyl-7,8-didehydrohydroshengmanol-3- <i>O</i> - α -L-arabinopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- <i>d</i> ₅	400	1.45	1.49	81.4	73.0	29
24- <i>O</i> -acetyl-7,8-didehydrohydroshengmanol-3- <i>O</i> - α -L-arabinopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- <i>d</i> ₅	400	1.47	1.48	82.6	71.3	29
24- <i>epi</i> -24- <i>O</i> -acetyl-7,8-didehydrohydroshengmanol-3- <i>O</i> - β -D-galactopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- <i>d</i> ₅	400	1.45	1.49	81.4	72.2	19
24- <i>O</i> -acetyl-7,8-didehydrohydroshengmanol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- <i>d</i> ₅	400	1.47	1.47	82.6	71.3	29
24- <i>O</i> -acetyl-7,8-didehydrohydroshengmanol-3- <i>O</i> - β -D-xylopyranoside	<i>heracleifolia</i>	Hydroxyshengmanol	Pyridine- <i>d</i> ₅	400	1.49	1.69	80.3	75.4	8
24- <i>epi</i> -24- <i>O</i> -acetyl-7,8-didehydrohydroshengmanol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- <i>d</i> ₅	400	1.47	1.50	81.4	72.2	29
24- <i>O</i> -acetyl-25- <i>O</i> -methyl-7,8-dehydroshengmanol-3- <i>O</i> - β -D-xylopyranoside	<i>simplex</i>	Hydroxyshengmanol	Pyridine- <i>d</i> ₅	500	1.21	1.27	79.5	76.3	30
24- <i>epi</i> -24- <i>O</i> -acetyl-7,8-dehydroshengmanol-3- <i>O</i> -(2'- <i>O</i> -malonyl)- β -D-xylopyranoside	<i>Simplex</i>	Hydroxyshengmanol	Pyridine- <i>d</i> ₅	500	1.48	1.52	81.3	72.0	30
podocarpaside G	<i>Podocarpa</i>	Podocarpaside	Chloroform- <i>d</i> ₃	400	1.45	1.45	56.2	69.8	37
podocarpaside A	<i>Podocarpa</i>	Podocarpaside	Chloroform- <i>d</i> ₃	400	1.49	1.50	56.1	69.8	37
podocarpaside B	<i>Podocarpa</i>	Podocarpaside	Chloroform- <i>d</i> ₃	400	1.47	1.49	56.2	69.9	37

Name Given in the Literature	Species	Structural Type	Solvent	Field	H-26	H-27	C-24	C-25	Ref
podocarpaside C	<i>Podocarpa</i>	Podocarposide	Chloroform- <i>d</i> ₃	400	1.45	1.46	56.1	69.7	37
podocarpaside D	<i>Podocarpa</i>	Podocarposide	Chloroform- <i>d</i> ₃	400	1.46	1.47	56.2	69.8	37
podocarpaside E	<i>Podocarpa</i>	Podocarposide	Chloroform- <i>d</i> ₃	400	1.48	1.48	56.1	69.8	37
podocarpaside F	<i>Podocarpa</i>	Podocarposide	Chloroform- <i>d</i> ₃	400	1.45	1.46	56.1	69.8	37

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S5: The Average Values (δ , in ppm) and Standard Deviations (σ) of the Chemical Shifts of H-26, H-27, C-24, C-25, and C-26 in the Ten Principal Types of *Actaea* Triterpenes.

new systematic name	common name	N^a	$\delta_{\text{H-26}}$ (σ)	$\delta_{\text{H-27}}$ (σ)	$\delta_{\text{C-24}}$ (σ)	$\delta_{\text{C-25}}$ (σ)	$\delta_{\text{C-26}}$ (σ)
(24 <i>R</i> ,25 <i>R</i>)-24,25-epoxyacta-(16 <i>S</i> ,23 <i>S</i>)-16,23;23,26-binoxol	26-deoxyacteol	10	–	1.46 (0.041)	62.6 (0.26)	62.4 (0.41)	68.1 (0.45)
(24 <i>R</i> ,25 <i>S</i>)-24,25-epoxy-(26 <i>S</i>)-26-hydroxy-acta-(16 <i>S</i> ,23 <i>R</i>)-16,23;23,26-binoxoside	26 β -hydroxyacteol	9	–	1.79 (0.042)	63.5 (0.14)	65.7 (0.21)	98.5 (0.16)
(24 <i>R</i> ,25 <i>S</i>)-24,25-epoxy-(26 <i>R</i>)-26-hydroxy-acta-(16 <i>S</i> ,23 <i>R</i>)-16,23;23,26-binoxoside	26 α -hydroxyacteol	3	–	1.56 (0.021)	62.9 (0.49)	64.1 (0.00)	97.8 (0.00)
(11 <i>S</i> ,15 <i>R</i>)-11,15-dihydroxy-(24 <i>R</i>)-24,25-epoxy-16,23-dioxoactanoside	cimicidanol	6	1.32 (0.024)	1.36 (0.014)	65.7 (0.11)	60.7 (0.24)	–
(15 <i>R</i>)-15,25-dihydroxyacta-(16 <i>S</i> ,23 <i>R</i> ,24 <i>S</i>)-16,23;16,24-binoxoside	cimigenol	28	1.46 (0.092)	1.49 (0.077)	89.8 (1.21)	71.1 (0.59)	–
(15 <i>R</i>)-15,25-dihydroxyacta-(16 <i>S</i> ,23 <i>R</i> ,24 <i>R</i>)-16,23;16,24-binoxoside	24- <i>epi</i> -cimigenol	8	1.28 (0.044)	1.40 (0.047)	83.8 (0.40)	68.7 (0.05)	–
25-acetoxy-(15 <i>R</i>)-15-hydroxyacta-(16 <i>S</i> ,23 <i>R</i> ,24 <i>S</i>)-16,23;16,24-binoxoside	25- <i>O</i> -acetylcimigenol	15	1.67 (0.027)	1.69 (0.029)	86.7 (0.18)	83.2 (0.19)	–
(23 <i>R</i> ,24 <i>R</i>)-23,24-dihydroxyacta-(16 <i>S</i> ,22 <i>R</i>)-16,23;22,25-binoxoside	cimiracemoside	11	1.68 (0.016)	1.77 (0.011)	83.4 (0.35)	83.8 (0.36)	–
(24 <i>S</i>)-24-acetoxy-(15 <i>R</i> ,16 <i>R</i>)-15,16,25-trihydroxyacta-(23 <i>S</i>)-16,23-monoxoside	hydroshengmanol	19	1.41 (0.132)	1.45 (0.129)	80.5 (1.41)	73.3 (1.92)	–
(23 <i>R</i>)-23-acetoxy-(24 <i>S</i>)-24,25-epoxy-(15 <i>R</i>)-15-hydroxy-16-oxoactanoside	23- <i>O</i> -acetylshengmanol	11	1.27 (0.024)	1.41 (0.021)	65.1 (0.09)	58.5 (0.14)	–

^a The total number of compounds used for the calculation.

S6: Experimental Details of the 1D and 2D-NMR Experiments.

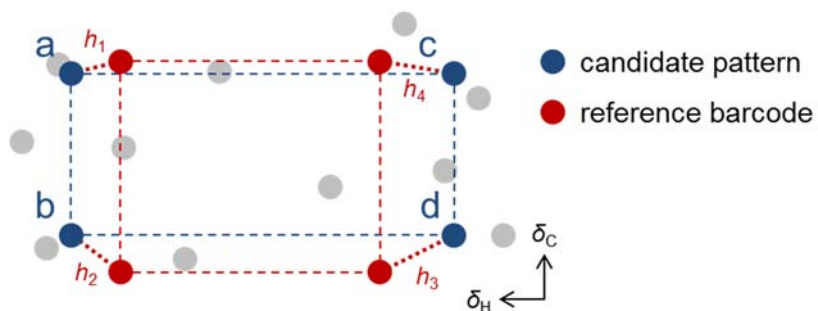
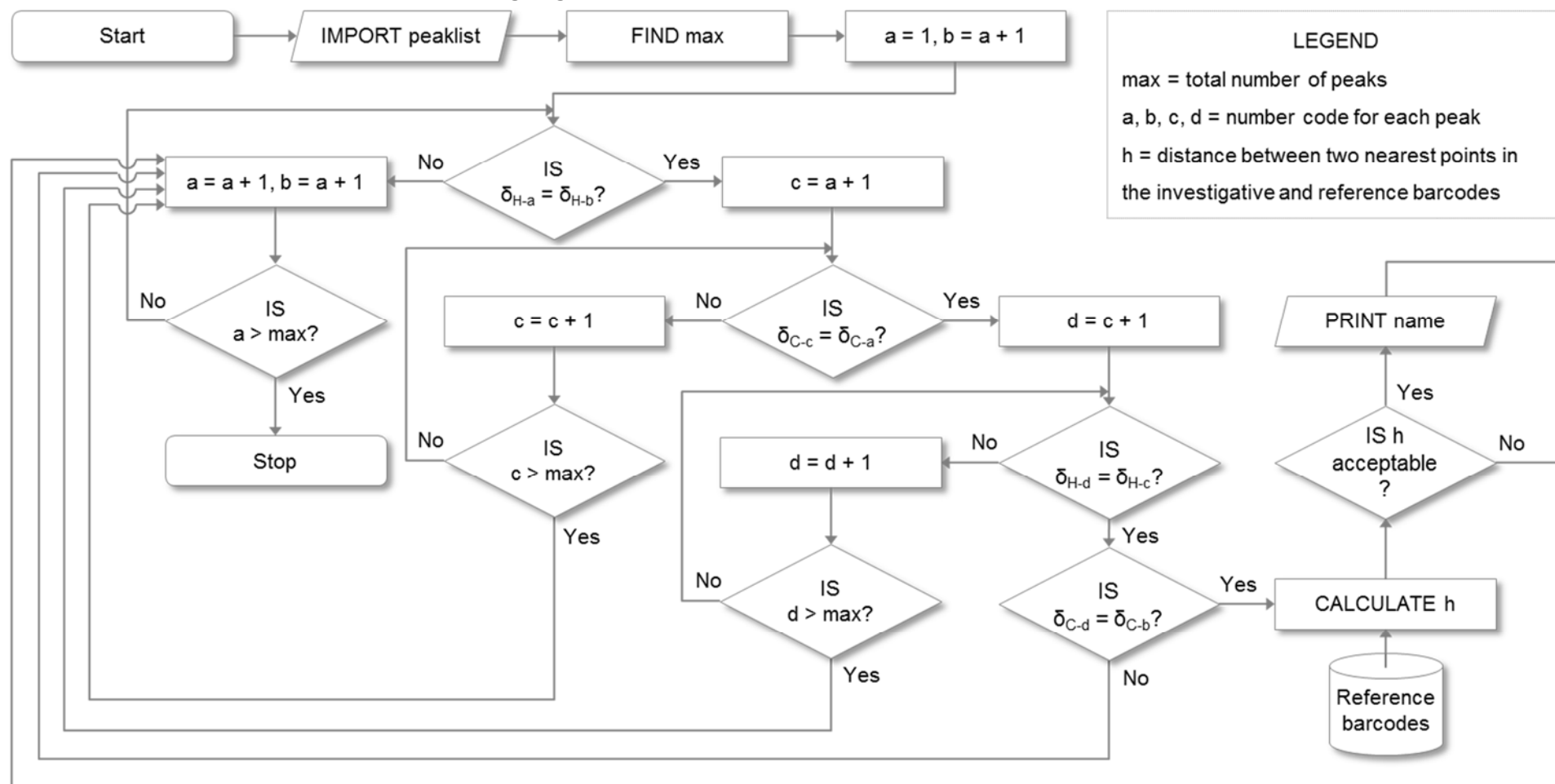
All NMR experiments were performed on a Bruker Avance-III 700 MHz NMR spectrometer equipped with a 1.7 mm cryo-microprobe (Bruker BioSpin, Karlsruhe, Germany). Each sample was thoroughly dissolved in 35 μL of pyridine-*d*₅ (99.96% D, Aldrich-Sigma, St. Louis, MO, USA) and transferred to a 1.7 mm NMR tube. The temperature of the sample was regulated at 293.2 K for all experiments.

The ¹H NMR spectra were acquired using the Bruker pulse program ‘zg30’ with ns = 128 scans, a receiver gain setting (rg) = 32, a relaxation delay (d1) = 2 s, a ¹H 90° pulse width (p1) = 12 μs , an acquisition time (aq) = 2.2719 s, a spectral width (sw) = 20.600 ppm, a transmitter offset (o1p) = 4.710 ppm, and an acquired data point size (td) = 32K. The spectra were processed using MestReNova v7.0.2-8636 software (Mestrelab Research, Santiago de Compostela, Spain). Spectral resolution was improved by Lorentzian-Gaussian window functions (LB = -2.0, GB = 0.10) with a zero filling to 64K complex points. For both 1D and 2D-NMR experiments, following Fourier transformation of the time domain signal, the frequency domain spectra were phased and baseline corrected (5th-order polynomial) as appropriate. Chemical shifts (δ , expressed in ppm) were referenced to the signals of residual pyridine at $\delta_{\text{H}} = 7.220$ ppm and $\delta_{\text{C}} = 123.87$ ppm, respectively.

The HSQC spectra were acquired using the Bruker pulse program ‘hsqcedetgp’, with ns = 2 scans per increment, a receiver gain setting (rg) = 203, a relaxation delay (d1) = 1.4781 s, a ¹H 90° pulse width (p1) = 12 μs , an acquisition time (aq) = 0.0768 s, spectral widths (sw) = 9.520 / 220.10 ppm (f2 / f1), transmitter offsets (o1p / o2p) = 4.370 / 100.80 ppm (f2 / f1), and acquired data point sizes (td) = 512 / 256 increments (f2 / f1). The spectral resolution in f2 was improved by a zero filling to 8K complex points along t2, followed by a linear prediction using the Toeplitz method with basis points 512 and coefficient 24.

The HMBC spectra were acquired using the Bruker pulse program: 'hmbcgp1pndqf', ns = 4 scans / increment, a receiver gain setting (rg) = 203, a relaxation delay (d1) = 0.9877 s, a ^1H 90° pulse width (p1) = 12 μs , an acquisition time (aq) = 0.1536 s, spectral widths (sw) = 9.520 / 165.60 ppm (f2 / f1), transmitter offsets (o1p / o2p) = 4.640 / 74.60 ppm (f2 / f1), and acquired data point sizes (td) = 1024 / 256 increments (f2 / f1). The spectral resolution in f2 was improved by a zero filling to 8K complex points along t2, also followed by a linear prediction using the Toeplitz method with basis points 999 and coefficient 24.

S7: The HMBC Barcode Search and Matching Algorithm



Workflow: The number (max) of peaks is initially determined after the peak list is imported to the ‘barcode reader’. Then, the spectrum is in silico scanned to locate all candidate patterns, i.e., rectangles with four cross-peaks as the vertices. As shown, each peak (a) is initially checked with other peaks (b) whether $\delta_{H-a} = \delta_{H-b}$. If ‘b’ is found, ‘a’ is further checked vs. remaining peaks (c) whether $\delta_{C-c} = \delta_{C-a}$. If ‘c’ is found, the remaining peaks (d) are checked whether $\delta_{H-d} = \delta_{H-c}$ and $\delta_{C-d} = \delta_{C-b}$. If ‘d’ is also found, a candidate pattern consisting of these four peaks (a, b, c, d) is determined. Finally, pattern matching is carried out by calculating the distance (h) between two nearest points (cross-peaks) in the candidate and reference barcodes. If $h < h_0$, the corresponding structure is assigned to the candidate barcode.

S8: The User Interface of the NMR Barcode Reader v1.0

The NMR Barcode Reader consists of two panels (Excel worksheets) in an XLSM file: **Sheet A** shows the peak list, the NMR spectra, and the match results. **Sheet B** stores the reference NMR barcodes of each chemical species.

Matching

REFERENCE BARCODES

#	Name	¹ H (ppm)	¹³ C (ppm)	Barcodes	Structure
1	26-deoxyactool	1.46	62.4	•	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
2	26β-hydroxyactool	1.79	63.5	•	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
3	26α-hydroxyactool	1.56	62.9	•	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
4	cimicidanol	1.32	65.7	••	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
5	cimgenol	1.46	89.0	••	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
6	24-epi-cimgenol	1.28	83.8	••	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
7	25-O-acetylcimgenol	1.67	86.7	•	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
8	cimracemoside	1.68	83.4	••	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
9	hydroshengmanol	1.41	80.5	••	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>
10	23-O-acetylshengmanol	1.27	65.1	••	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>

PEAKLIST

¹ H (ppm)	¹³ C (ppm)	Hits
1.804	65.81	***
1.786	67.44	***
1.786	65.82	***
1.786	63.63	***
1.785	98.65	***
1.783	68.38	***
1.768	77.32	**
1.768	65.71	**
1.764	83.79	*
1.737	56.62	*
1.695	56.52	*
1.693	83.94	*
1.688	83.45	*
1.674	56.56	*
1.667	63.63	*
1.663	80.25	*
1.652	56.62	*
1.635	98.40	*
1.634	63.99	*
1.609	82.80	*
1.546	73.25	*
1.525	82.04	*
1.522	80.32	*
1.501	71.30	*
1.483	82.92	**
1.482	71.41	**
1.467	82.90	**
1.466	71.40	**
1.445	84.32	**
1.445	68.72	**
1.413	58.81	**
1.395	65.38	**
1.395	58.79	**
1.394	60.45	**
1.376	58.74	**
1.370	60.19	**
1.362	77.30	***
1.362	74.73	***
1.362	56.61	***
1.360	54.91	***
1.359	58.39	***
1.358	75.60	***
1.348	58.69	***
1.347	60.06	***
1.346	77.30	***
1.346	56.47	***
1.342	65.59	***
1.339	58.63	***
1.339	68.74	***

2D HMBC

INSTRUCTIONS

- S1: Export - Export the HMBC peak list in .xlsx from NMR processing software
- S2: Import - Import the peak list into NMR Barcode Reader
- S3: Scan - Scan the HMBC to find candidate patterns and match them with the reference barcodes

Match

Updated: 01/27/2014

MATCHES

Pattern	¹ H (ppm)	¹³ C (ppm)	Best Match	Structure	Score
1	1.786	67.44			
2	1.786	65.82			
3	1.786	67.44			
4	1.786	65.82			
5	1.786	65.82	26β-hydroxyactool	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>	0.212
6	1.786	63.63	26β-hydroxyactool	<chem>C1=CC=C(C=C1)O[C@H]2[C@@H](O)[C@H](O)[C@@H](O)[C@H]2O</chem>	0.385
7	1.785	98.65			

Sheet A

Sheet B

Workflow: (1) The peak list is imported to Sheet A, and then each cross-peak is automatically displayed as blue dots in the 2D spectra. (2) The dotted lines are added by the macro program to indicate all candidate patterns (grey) and the matches (red) to the reference barcodes which are stored in Sheet B. (3) The match results are given, together with the names and structures of the corresponding chemical species.