Electronical Supporting Information

Trimeric Natural Products: Structural diversity, biosynthesis, bioactivities and chemical synthesis

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Contents

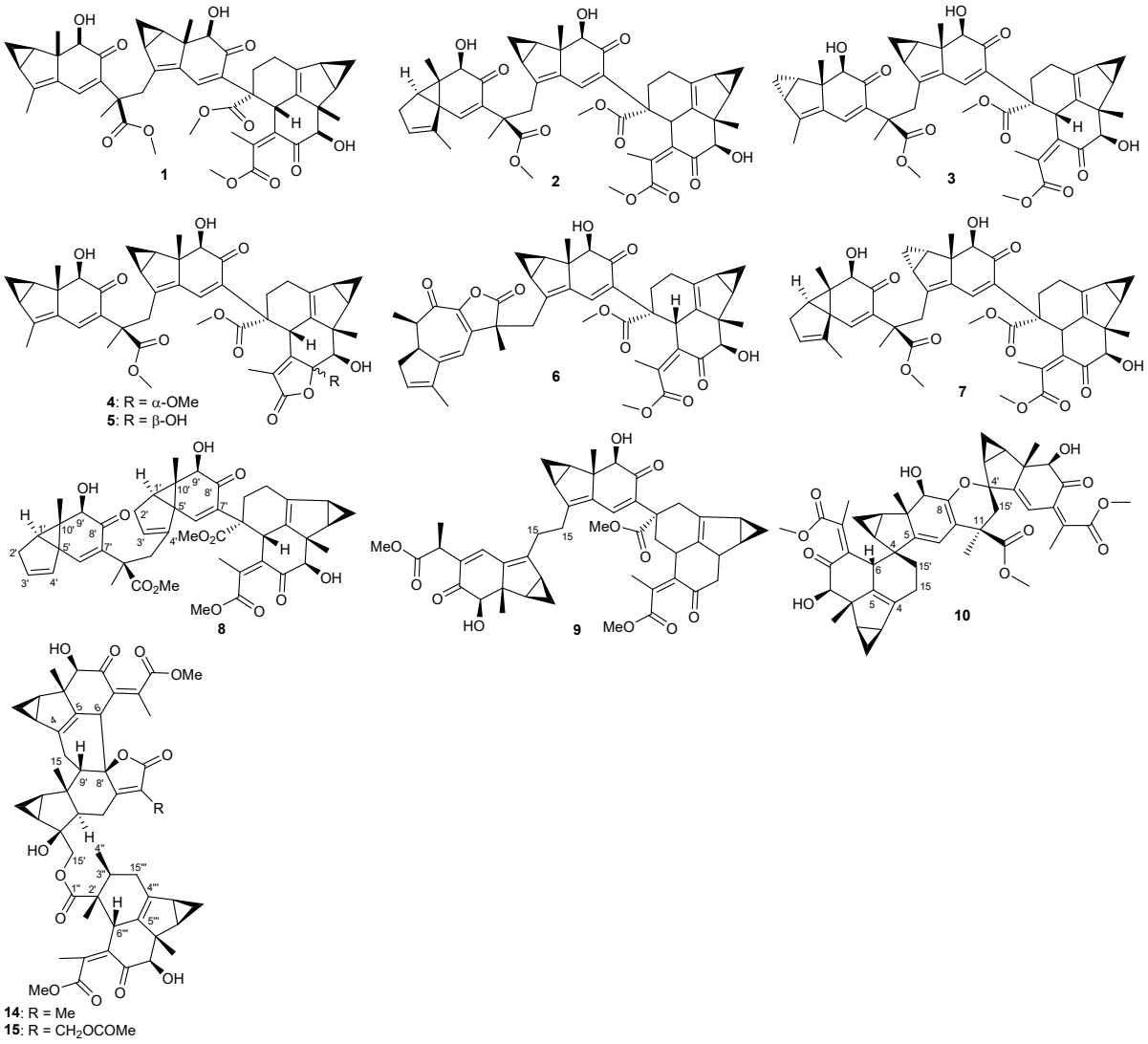
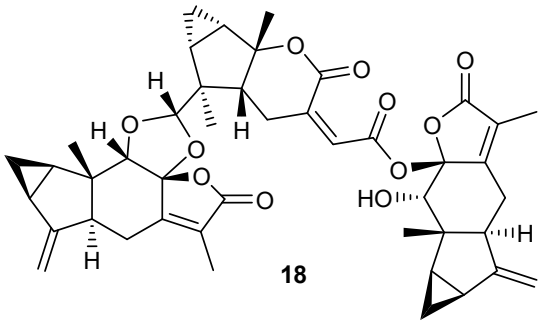
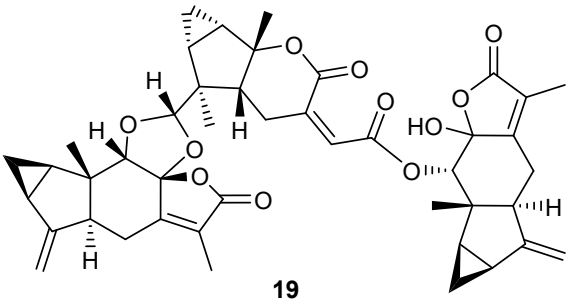


Table S1 Structure names, sources and bioactivity of sesquiterpene trimers **1-10**, **14** and **15**

No	Compound	Sources	Bioactivity
1	Trishizukaol A	*Chloranthus japonicus,*[1] *C. spicatus*[2], *C. fortune*[3]	Antimalarial[2]
2	Trichloranoid A	*C. spicatus*[2]	Antimalarial[2] Anti-inflammatory[3]
3	Trichloranoid B	*C. spicatus*[2]	Anti-inflammatory[3]
4	Trichloranoid C	*C. spicatus*[2]	
5	Trichloranoid D	*C. spicatus*[2]	Antimalarial[2]
6	Chlofortunin B	*C. fortune*[3]	Anti-inflammatory[3]
7	Chlofortunin C	*C. fortune*[3]	Anti-inflammatory[3]
8	Chlofortunin D	*C. fortune*[3]	Anti-inflammatory[3]
9	Chlofortunin A	*C. fortune*[3]	
10	Spirolindemer B	*C. henryi*[4]	
14	Trisarcglaboid A	*Sarcandra glabra*[5]	Cytotoxicity[5]
15	Trisarcglaboid B	*S. glabra*[5]	Cytotoxicity[5]



18



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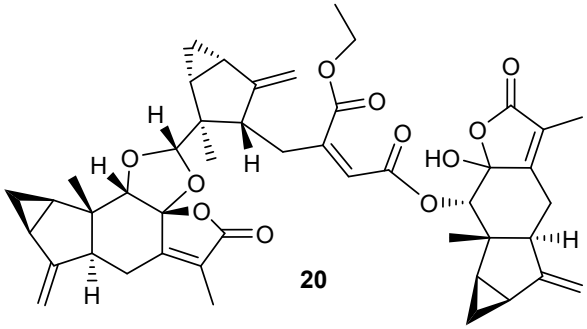

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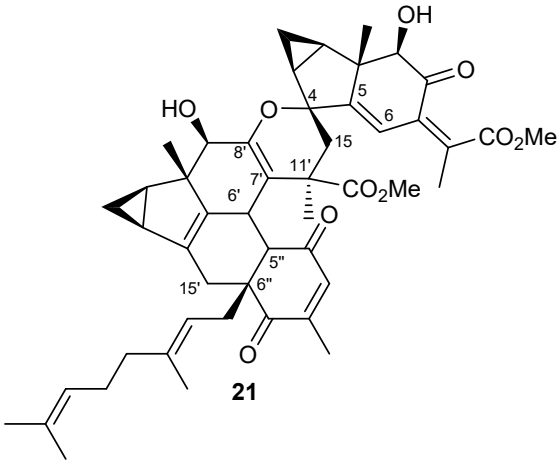


21

Table S2 Structure names, sources and bioactivity of trimers **18-21**

No	Compound	Sources	Bioactivity
18	Sarglactone A	*Sarcandra glabra*[6]	Cytotoxicity[6]
19	Sarglalactone B	*S. glabra*[6]	Cytotoxicity[6]
20	Sarglalactone C	*S. glabra*[6]	Cytotoxicity[6]
21	Holotrichone B	*Chloranthus holostegius*[7]	Cytotoxicity[7]

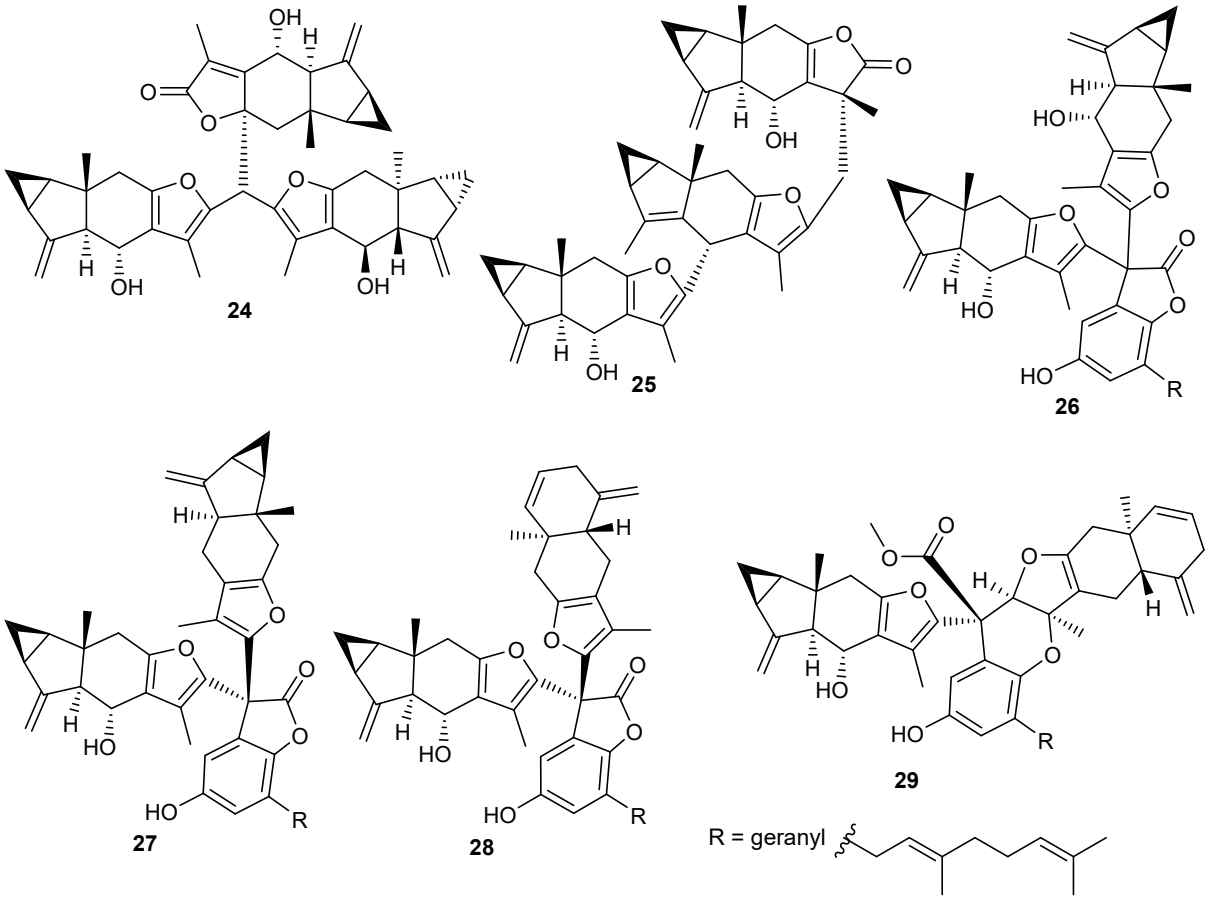
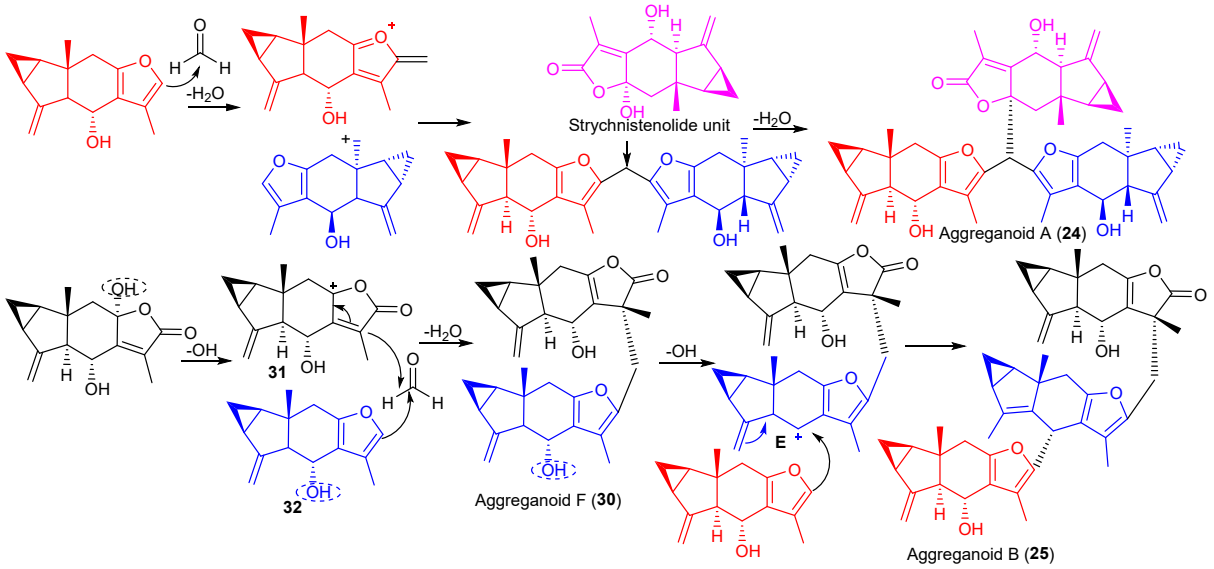
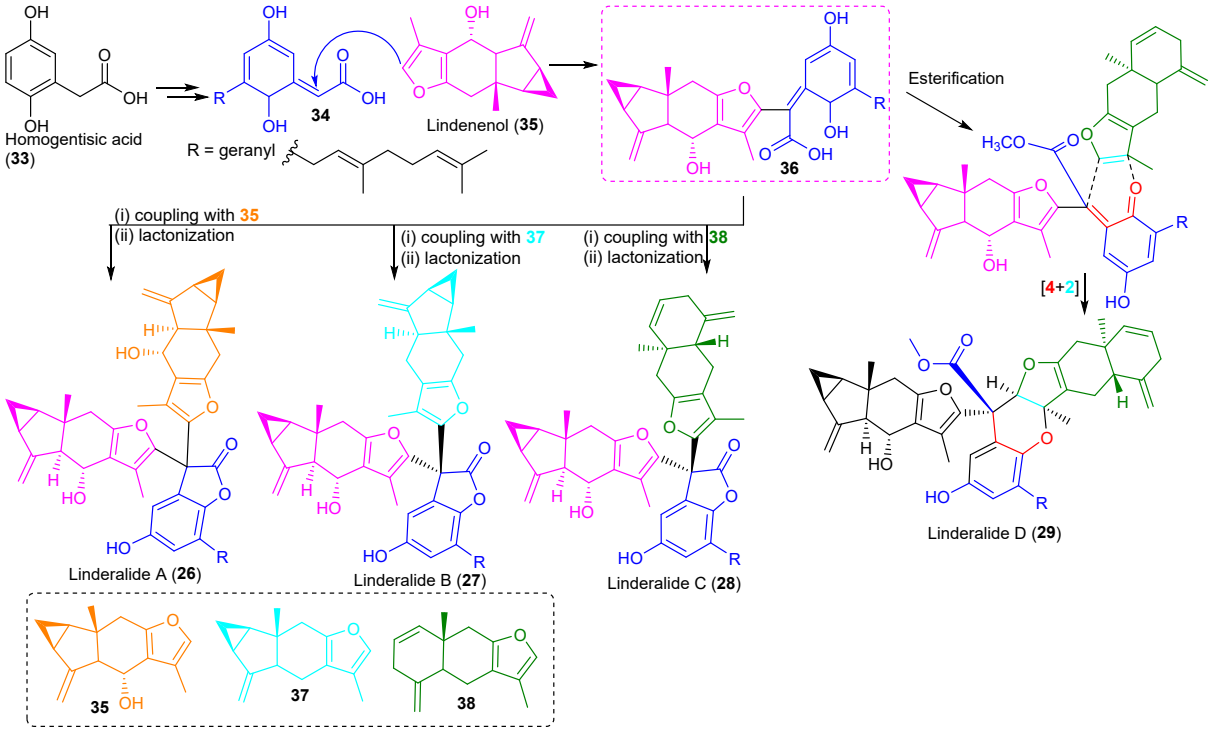


Table S3 Structure names, sources and bioactivity of trimers **24-29**.

No	Compound	Sources	Bioactivity
24	Aggreganoid A	*Lindera aggregata*[8]	TGF-b-Inhibitory[8]
25	Aggreganoid B	*L. aggregata*[8]	
26	Linderalide A	*L. aggregata*[9]	
27	Linderalide B	*L. aggregata*[9]	
28	Linderalide C	*L. aggregata*[9]	
29	Linderalide D	*L. aggregata*[9]	Anti-inflammatory[9]



Scheme S1 Biosynthesis of aggreganoids A (**24**) and B (**25**). Reproduced from ref. 8 with permission from the American Chemical Society.



Scheme S2 Biosynthesis of linderalides A–D (**26-29**). Reproduced from ref. 9 with permission from the American Chemical Society.

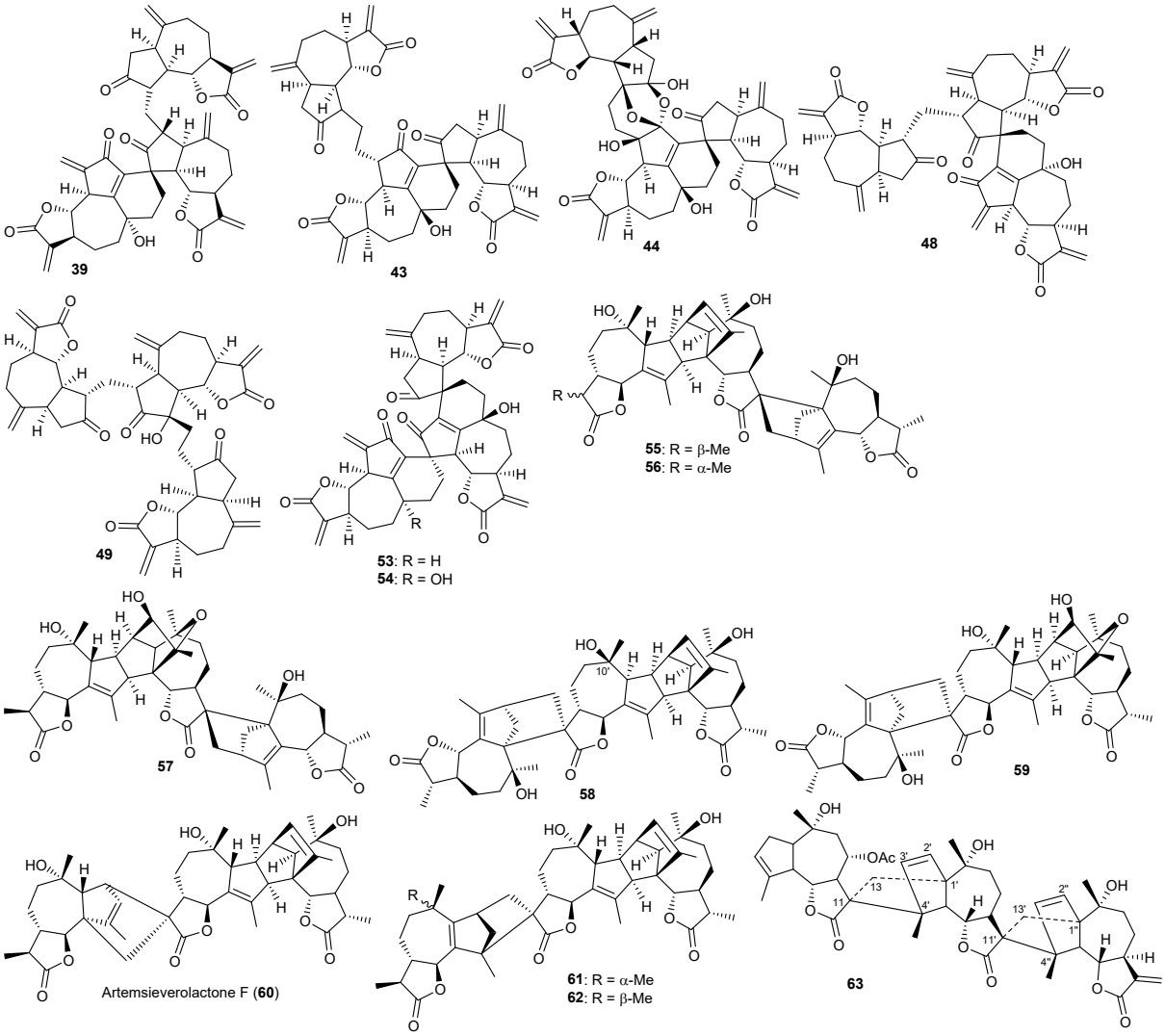
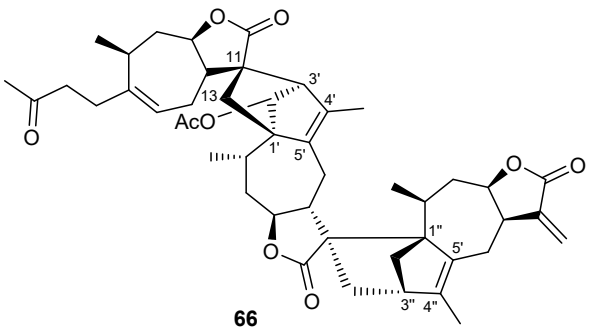


Table S4 Structure names, sources and bioactivity of trimers **39**, **43**, **44**, **48**, **49**, **53-63**.

No	Compound	Sources	Bioactivity
39	Ainsfragolide	*Ainsliaea fragrans*[10]	Cytotoxicity[10]
43	Ainsliatriolide A	*Ainsliaea fragrans*[11]	Cytotoxicity[11]
44	Ainsliatriolide B	*Ainsliaea fragrans*[11]	Cytotoxicity[11]
48	Macrocephatriolide A	*Ainsliaea macrocephala*[12]	
49	Macrocephatriolide B	*Ainsliaea macrocephala*[12]	PTP1B inhibition[12]
53	(-)-Ainsliatrimer A	*Ainsliaea fulvioides*[13]	Cytotoxicity[13]
54	(-)-Ainsliatrimer B	*Ainsliaea fulvioides*[13]	Cytotoxicity[13]
55	Artemsieverolactone A	*Artemisia sieversiana*[14]	Anti-hepatic[14]
56	Artemsieverolactone B	*Artemisia sieversiana*[14]	Anti-hepatic[14]
57	Artemsieverolactone C	*Artemisia sieversiana*[14]	Anti-hepatic[14]
58	Artemsieverolactone D	*Artemisia sieversiana*[14]	Anti-hepatic[14]
59	Artemsieverolactone E	*Artemisia sieversiana*[14]	
60	Artemsieverolactone F	*Artemisia sieversiana*[14]	Anti-hepatic[14]
61	Artemsieverolactone G	*Artemisia sieversiana*[14]	Anti-Hepatic[14]
62	Artemsieverolactone H	*Artemisia sieversiana*[14]	
63	Chrysanolide A	*Chrysanthemum indicum*[15]	



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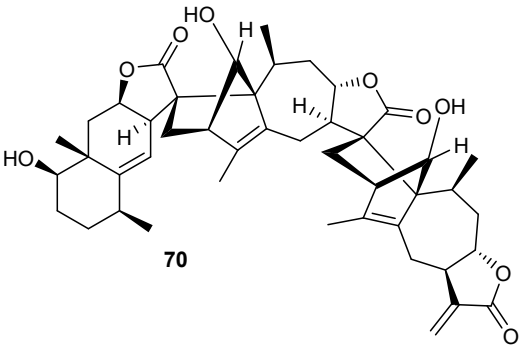
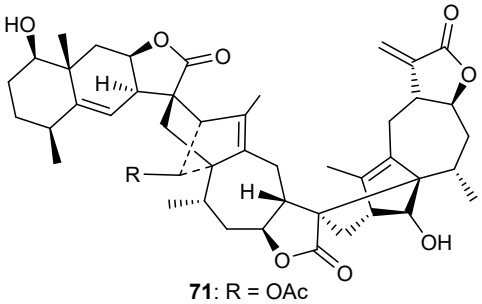
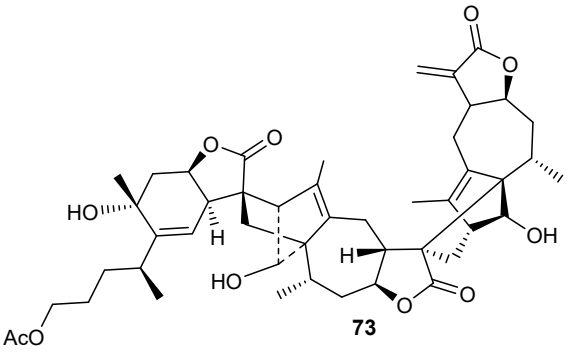


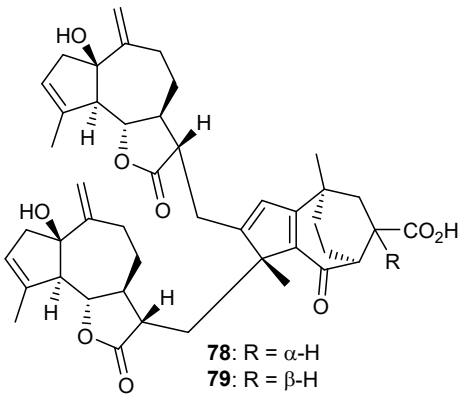
70



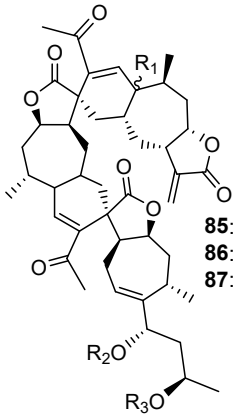
71: R = OAc
72: R = OH



73



78: R = α-H
79: R = β-H



85: R_1 = α-OH, R_2 = H, R_3 = Ac
86: R_1 = α-OH, R_2 = Ac, R_3 = H
87: R_1 = β-OH, R_2 = H, R_3 = Ac

Table S5 Structure names, sources and bioactivity of trimers **66**, **70-73**, **78-79**, **85-87**

No	Compound	Sources	Bioactivity
66	Inulajaponicolide A	*Inula japonica*[16]	Anti-inflammatory[16]
70	Inubritantrimer A	*Inula britannica*[17]	Cytotoxicity[17]
71	Inubritantrimer B	*Inula britannica*[17]	Cytotoxicity[17]
72	Inubritantrimer C	*Inula britannica*[17]	Cytotoxicity[17]
73	Inubritantrimer D	*Inula britannica*[17]	Cytotoxicity[17]
78	Artematrotrimer A	*Artemisia atrovirens*[18]	
79	Artematrotrimer B	*Artemisia atrovirens*[18]	
85	Xanthanoltrimer A	*Xanthium italicum*[19]	
86	Xanthanoltrimer B	*Xanthium italicum*[19]	
87	Xanthanoltrimer C	*Xanthium italicum*[19]	

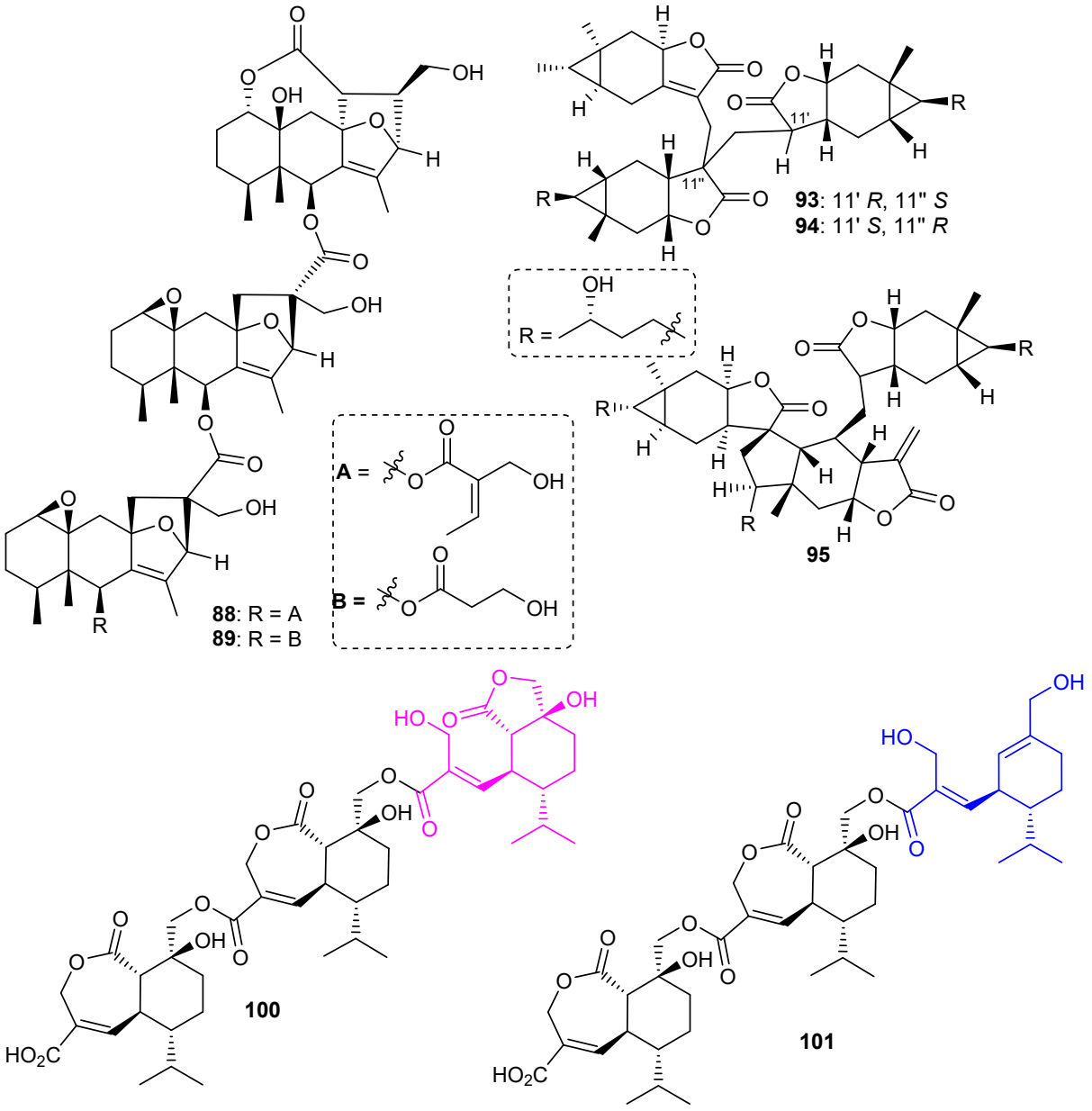


Table S6 Structure names, sources and bioactivity of trimers **88-89**, **93-95, 100-101**.

No	Compound	Sources	Bioactivity
88	Ligusaginoid C	*Ligularia sagitta*[20]	
89	Ligusaginoid D	*Ligularia sagitta*[20]	
93	Tricarabrol A	*Carpesium faberi*[21]	Anti-inflammatory[21]
94	Tricarabrol B	*Carpesium faberi*[21]	Anti-inflammatory[21]
95	Tricarabrol C	*Carpesium faberi*[21]	
100	Trivirensol A	*Trichoderma virens*[22]	Antimicrobial[22]
101	Trivirensol B	*Trichoderma virens*[22]	Antimicrobial[22]

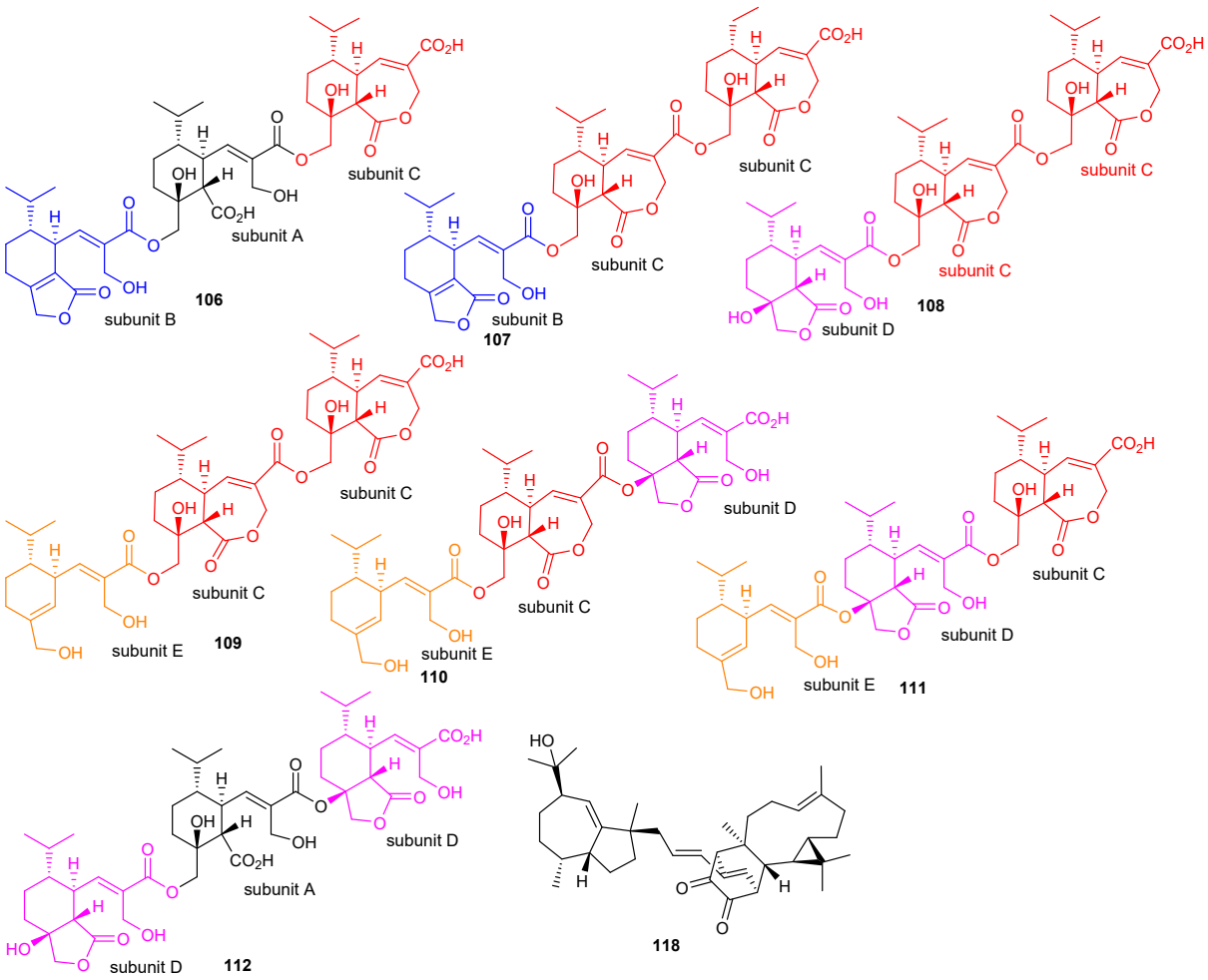


Table S7 Structure names, sources and bioactivity of trimers **106**-**112**, **118**.

No	Compound	Sources	Bioactivity
106	Trivirensol A	*Trichoderma virens*[23]	Antimicrobial[23]
107	Trivirensol B	*Trichoderma virens*[23]	Antimicrobial[23]
108	Trivirensol C	*Trichoderma virens*[23]	Antimicrobial[23]
109	Trivirensol D	*Trichoderma virens*[23]	Antimicrobial[23]
110	Trivirensol E	*Trichoderma virens*[23]	Antimicrobial[23]
111	Trivirensol F	*Trichoderma virens*[23]	Antimicrobial[23]
112	Trivirensol G	*Trichoderma virens*[23]	Antimicrobial[23]
118	Nudibaccatumone	*Piper nudibaccatum*[24]	

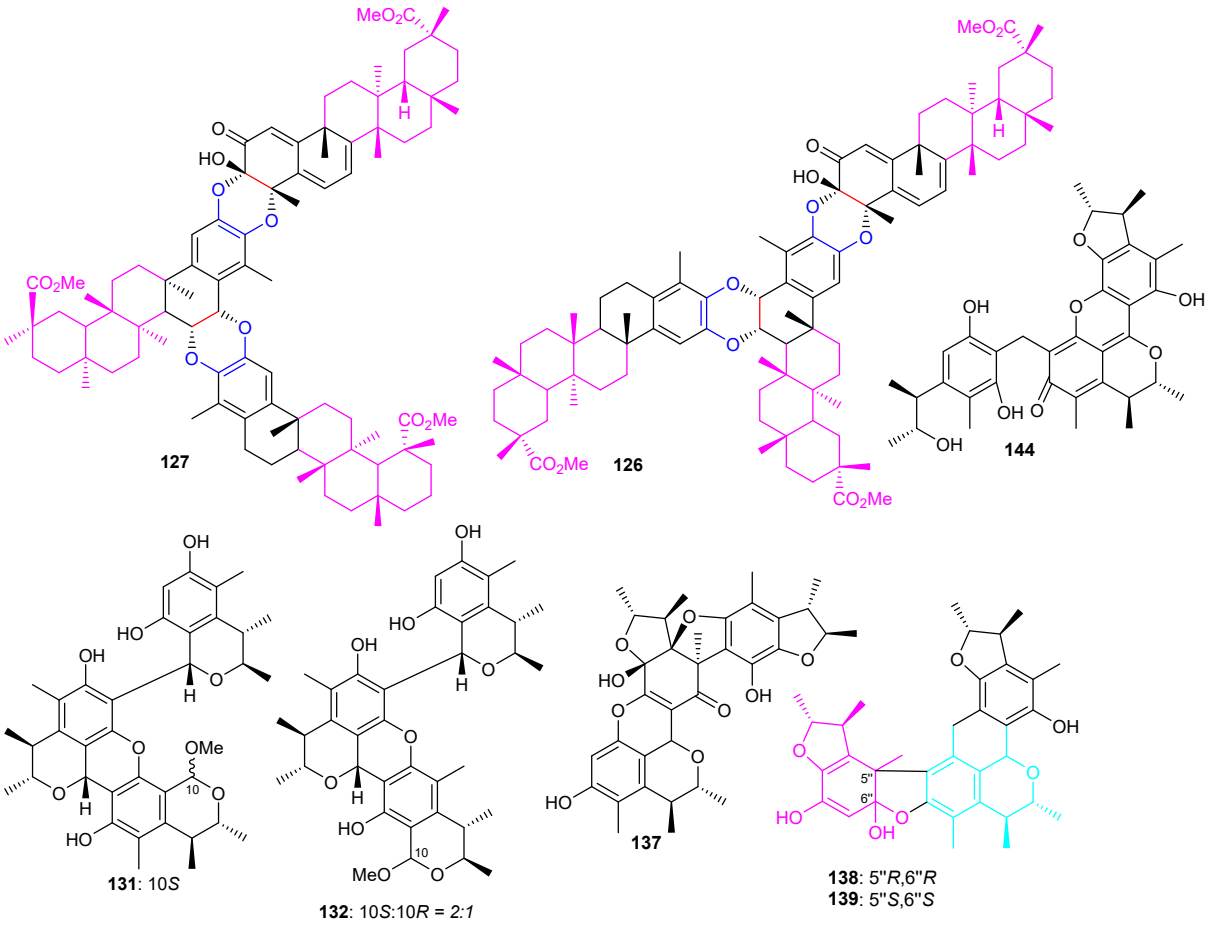


Table S8 Structure names, sources and bioactivity of trimers **126**-**127**, **131**-**132, 137**-**139**, **144**.

No	Compound	Sources	Bioactivity
126	Triscutin A	*Maytenus scutioides*[25]	
127	Triscutin B	*Maytenus scutioides*[25]	
131	Tricitrinol A	*Penicillium citrinum*[26]	Cytotoxicity[26]
132	Tricitrinol B	*Penicillium citrinum*[26]	Cytotoxicity[26]
137	Neotricitrinol A	*Penicillium citrinum*[27]	
138	Neotricitrinol B	*Penicillium citrinum*[27]	Anti-osteoporotic[27]
139	Neotricitrinol C	*Penicillium citrinum*[27]	
144	Tricitrinol C	*Penicillium citrinum*[28]	Cytotoxicity[28]

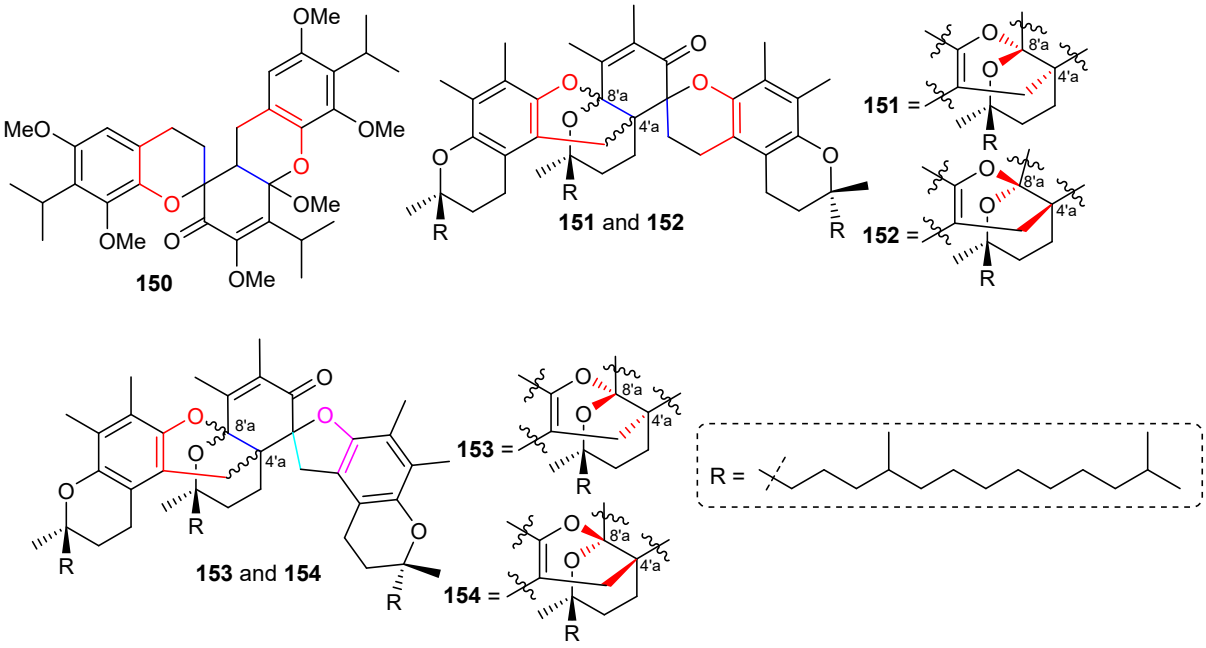


Table S9 Structure names, sources and bioactivity of trimers **150**-**154**.

No	Compound	Sources	Bioactivity
150	(±)-Schefflone	*Uvaria schefflera*[29]	
151	Trimer IVb	*Euryale ferox*[30]	
152	Trimer IVa	*Euryale ferox*[30]	
153	Ferotocotrimer C	*Euryale ferox*[30]	
154	Ferotocotrimer D	*Euryale ferox*[30]	

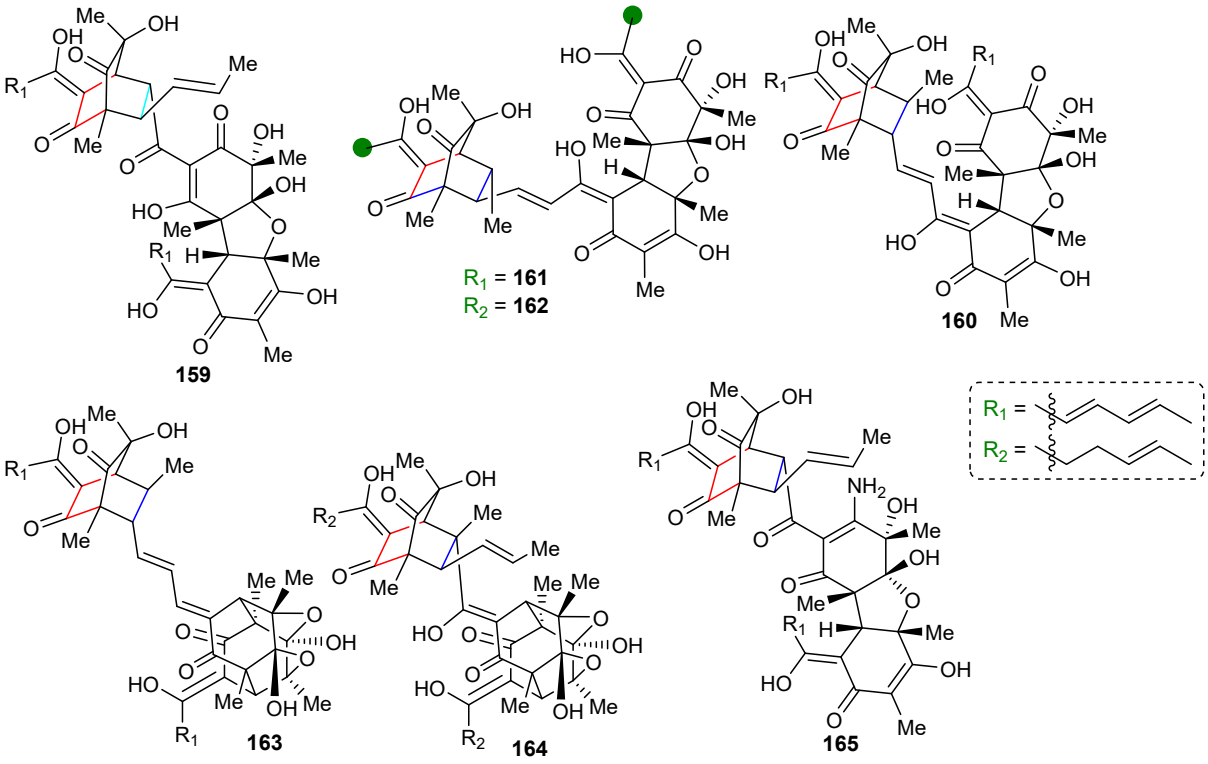


Table S10 Structure names, sources and bioactivity of trimers **159**-**165**.

No	Compound	Sources	Bioactivity
159	Trisorbicillinone A	*Phialocephala sp.* FL30r[31]	Cytotoxicity[31]
160	Trisorbicillinone B	*Phialocephala sp.* FL30r[32]	Cytotoxicity[32]
161	Trisorbicillinone C	*Phialocephala sp.* FL30r[32]	Cytotoxicity[32]
162	Tetrahydrotrisorbicillinone C	*Penicillium chrysogenum 581F1*[33]	Antidiabetic[33] Cytotoxicity[33]
163	Trisorbicillinone D	*Phialocephala sp.* FL30r[32]	Cytotoxicity[32]
164	Trisorbicillinone E	*Phialocephala sp.* FL30r[34]	Cytotoxicity[34] Antimicrobial[34]
165	Sorbicillamine E	*Penicillium sp. F232*[35]	Cytotoxicity[35]

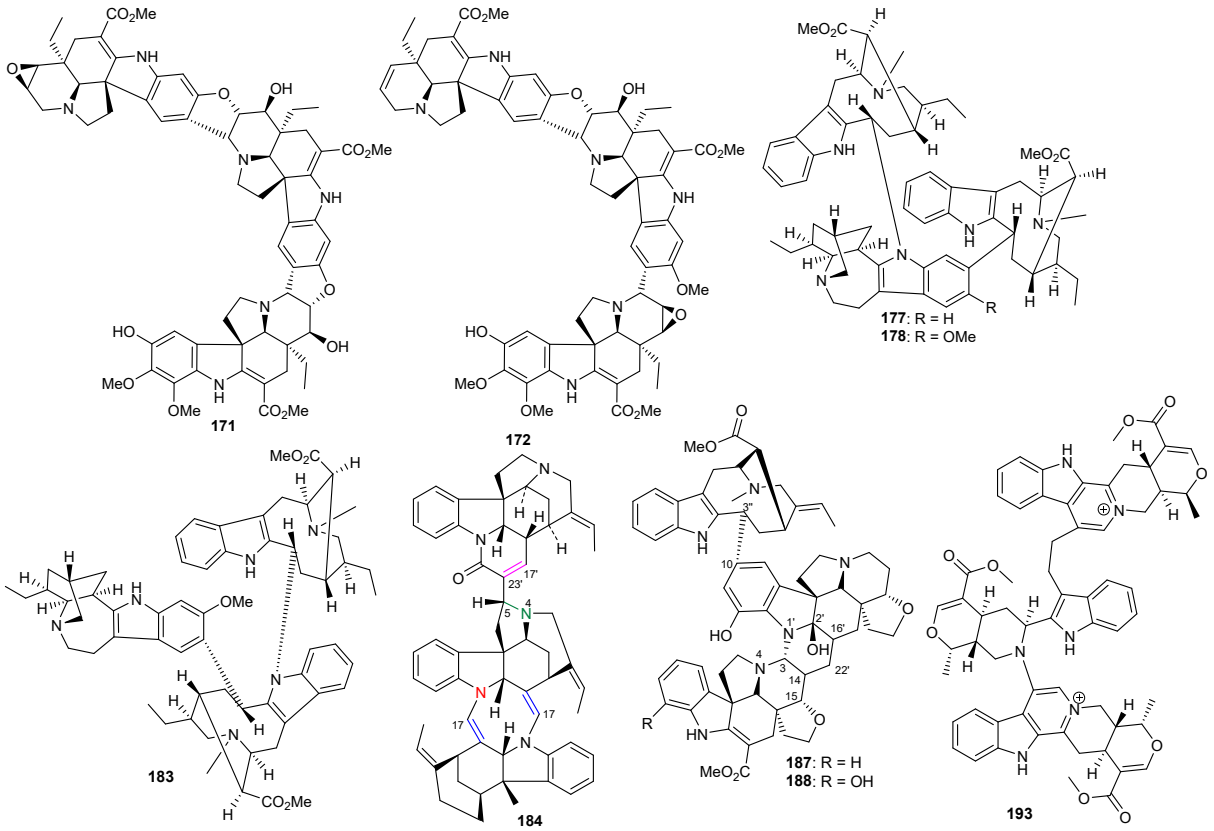


Table S11 Structure names, sources and bioactivity of trimers **171**-**172**, **177**-**178**, **183**-**184**, **187**-**188**, **193**.

No	Compound	Sources	Bioactivity
171	Taberdivarine A	*Tabernaemontana divaricata*[36]	Cytotoxicity[36]
172	Taberdivarine B	*Tabernaemontana divaricata*[36]	
177	Ervadivamine A	*Ervatamia divaricate*[37]	Cytotoxicity[37]
178	Ervadivamine A	*Ervatamia divaricate*[37]	
183	Divaricamine A	*Tabernaemontana divaricata*[38]	
184	Strychnohexamine	*Strychnos icaja*[39]	
187	Voatriafricanine A	*Voacanga africana*[40]	Antimicrobial[40]
188	Voatriafricanine B	*Voacanga africana*[40]	
193	Trirosaline	*Catharanthus roseus*[41]	

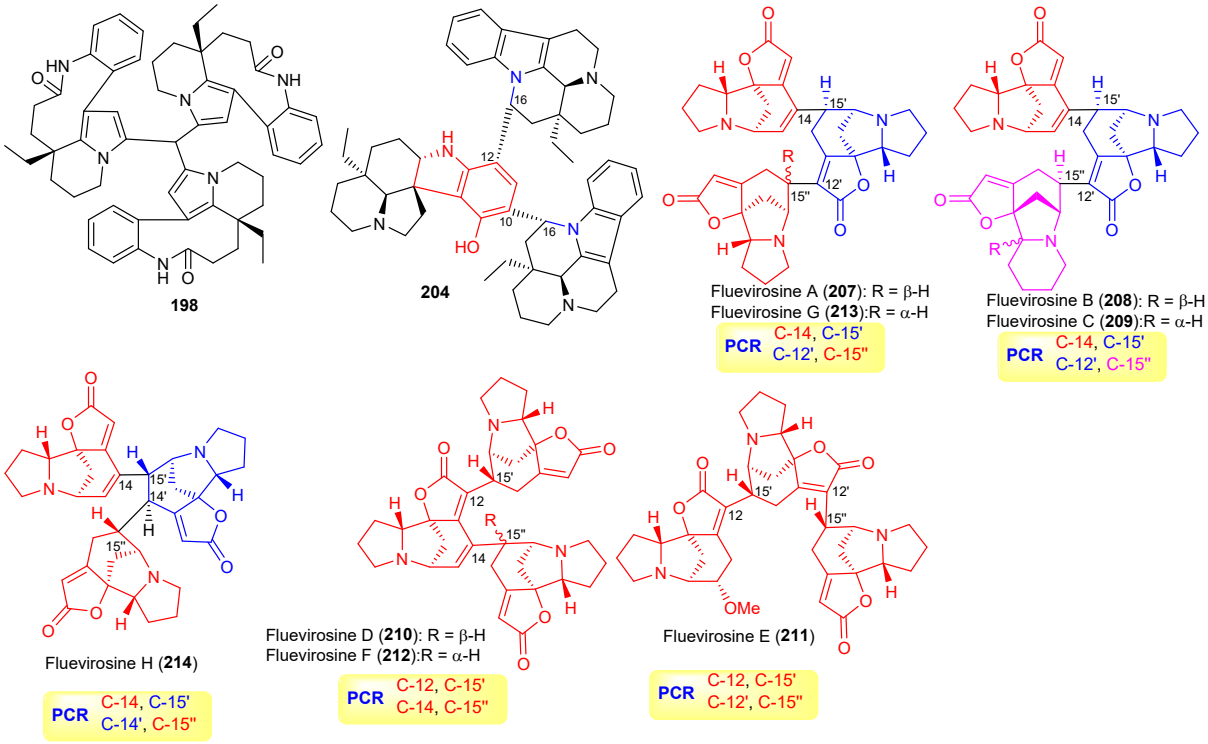
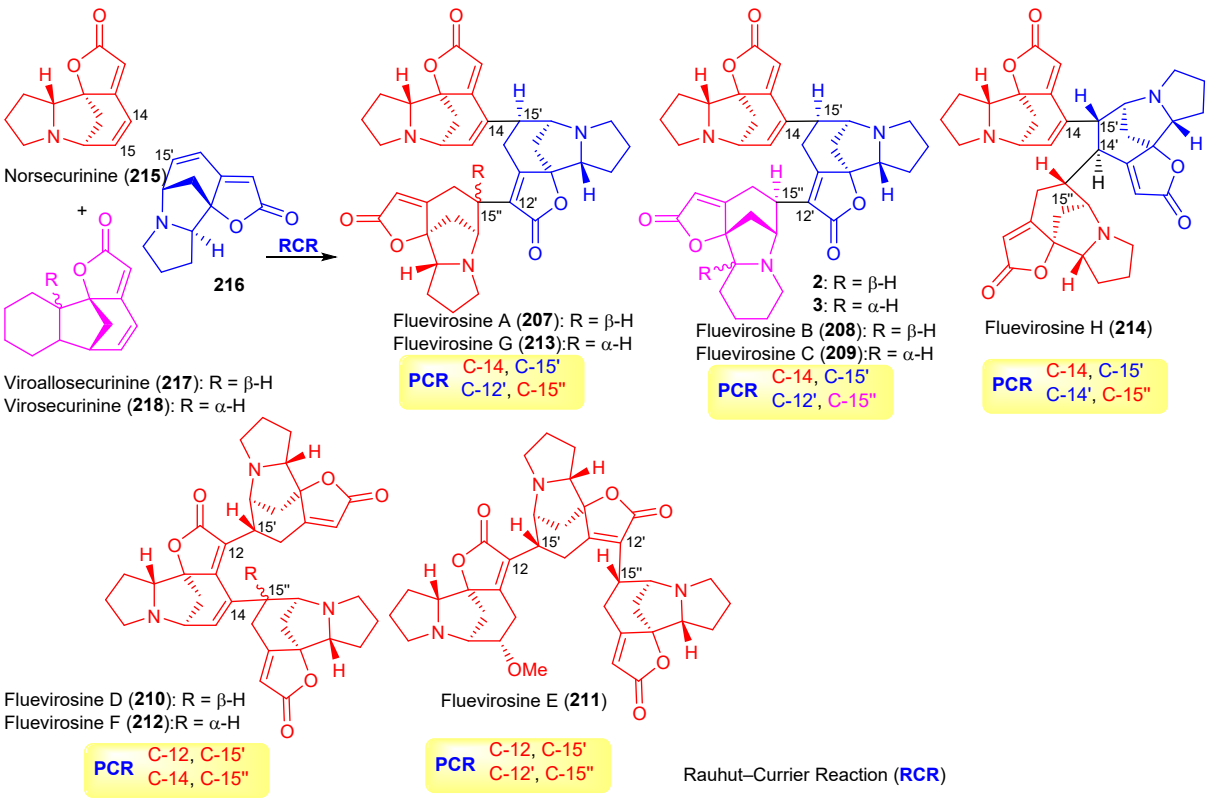


Table S12 Structure names, sources and bioactivity of trimers **198**, **204**, **208**-**214**.

No	Compound	Sources	Bioactivity
198	Bousangustine A	*Bousigonia angustifolia*[42]	Cytotoxicity[42]
204	Bousigonine B	*Bousigonia mekongensis*[43]	
207	Fluevirosine A	*Flueggea virosa*[44]	
208	Fluevirosine B	*Flueggea virosa*[44]	Inhibition of XBP1 mRNA (cancer)[44]
209	Fluevirosine C	*Flueggea virosa*[44]	Inhibition of XBP1 mRNA (cancer)[44]
210	Fluevirosine D	*Flueggea virosa*[45]	
211	Fluevirosine E	*Flueggea virosa*[46]	
212	Fluevirosine F	*Flueggea virosa*[46]	Anti-HIV[46]
213	Fluevirosine G	*Flueggea virosa*[46]	Anti-HIV[46]
214	Fluevirosine H	*Flueggea virosa*[46]	



Scheme S3 Biosynthesis of securinega alkaloid trimers **207-214**.

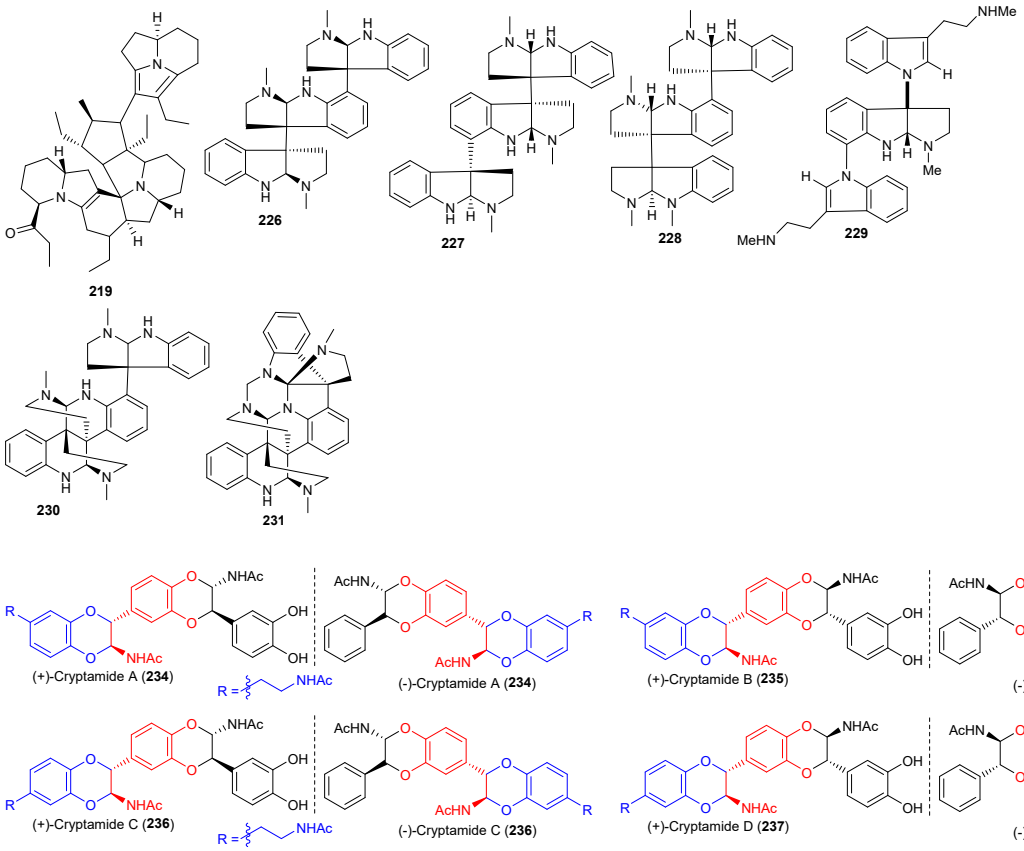
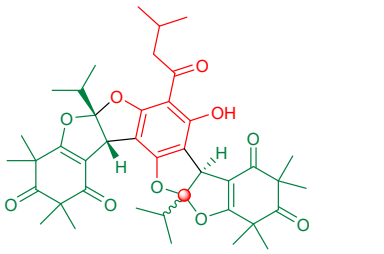
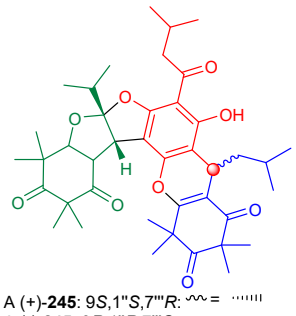


Table S13 Structure names, sources and bioactivity of trimers **219**, **226-231, 234-237**.

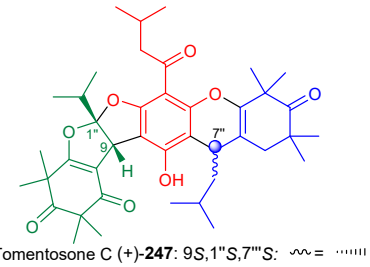
No	Compound	Sources	Bioactivity
219	Myrmicarin 663	*Myrmicaria* ant.[47]	
226	Hodgkinsine	*Psychotria colorata*[48]	Analgesic[48] Anti-inflammatory[49] Antimicrobial[49]
227	Hodgkinsine B	*Hodgkinsonia frutescens*[50]	
228	(-) Idiospermuline	*Idiospermum australiense*[51]	
229	Psychotrimine	*Psychotria rostrata*[52]	Antimicrobial[53]
230	Calycosidine	*Psychotria* sp.[54,55]	
231	Psychotripine	*Psychotria pilifera*[56]	
234	Cryptamide A	*Cryptotympana pustulata*[57]	
235	Cryptamide B	*Cryptotympana pustulata*[57]	Anti-inflammatory[57]
236	Cryptamide C	*Cryptotympana pustulata*[57]	Anti-inflammatory[57]
237	Cryptamide D	*Cryptotympana pustulata*[57]	Anti-inflammatory[57]



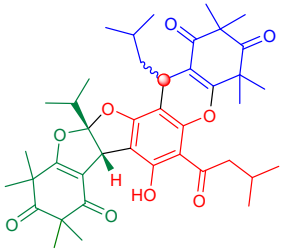
Rhodomentosone A (+)-**238a**/(-)-**238a**:
Rhodomentosone B (+)-**239a**/(-)-**239a**:



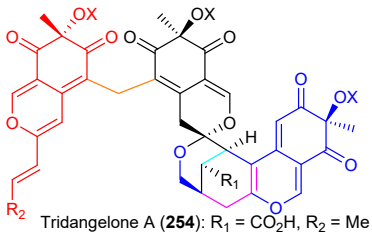
Tomentosone A (+)-**245**: 9*S*,1"*S*,7'''*R*:
Tomentosone A (-)-**245**: 9*R*,1"*R*,7'''*S*:
Tomentosone B (+)-**246**: 9*R*,1"*R*,7'''*R*:
Tomentosone B (-)-**246**: 9*S*,1"*S*,7'''*S*:



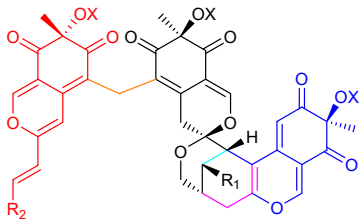
Tomentosone C (+)-**247**: 9*S*,1"*S*,7'''*S*:
Tomentosone C (-)-**247**: 9*R*,1"*R*,7'''*R*:
Tomentosone D (+)-**248**: 9*S*,1"*S*,7'''*S*:
Tomentosone D (-)-**248**: 9*R*,1"*R*,7'''*R*:



Tomentosone E (+)-**249**: 9*R*,1"*R*,7'''*S*:
Tomentosone E (-)-**249**: 9*S*,1"*S*,7'''*R*:
Tomentosone F (+)-**250**: 9*R*,1"*R*,7'''*R*:
Tomentosone F (-)-**250**: 9*S*,1"*S*,7'''*S*:



Tridangelone A (**254**): R_1 = CO_2H, R_2 = Me
Tridangelone C (**256**): R_1 = CO_2H, R_2 = CH_2OH
Tridangelone E (**258**): R_1 = R_2 = CH_2OH



Tridangelone B (**255**): R_1 = CO_2H, R_2 = Me
Tridangelone D (**257**): R_1 = CO_2H, R_2 = CH_2OH

Table S14 Structure names, sources and bioactivity of trimers **238-239**, **245-250**, **254-258**.

No	Compound	Sources	Bioactivity
238	Rhodomentosone A	*Rhodomyrtus tomentosa*[58]	
239	Rhodomentosone B	*Rhodomyrtus tomentosa*[58]	
245	Tomentosone A	*Rhodomyrtus tomentosa*[59]	
246	Tomentosone B	*Rhodomyrtus tomentosa*[59]	
247	Tomentosone C	*Rhodomyrtus tomentosa*[59]	
248	Tomentosone D	*Rhodomyrtus tomentosa*[59]	
249	Tomentosone E	*Rhodomyrtus tomentosa*[59]	
250	Tomentosone F	*Rhodomyrtus tomentosa*[59]	
254	Tridangelone A	*Penicillium dangeardii*[60]	
255	Tridangelone B	*Penicillium dangeardii*[60]	
256	Tridangelone C	*Penicillium dangeardii*[60]	
257	Tridangelone D	*Penicillium dangeardii*[60]	
258	Tridangelone E	*Penicillium dangeardii*[60]	

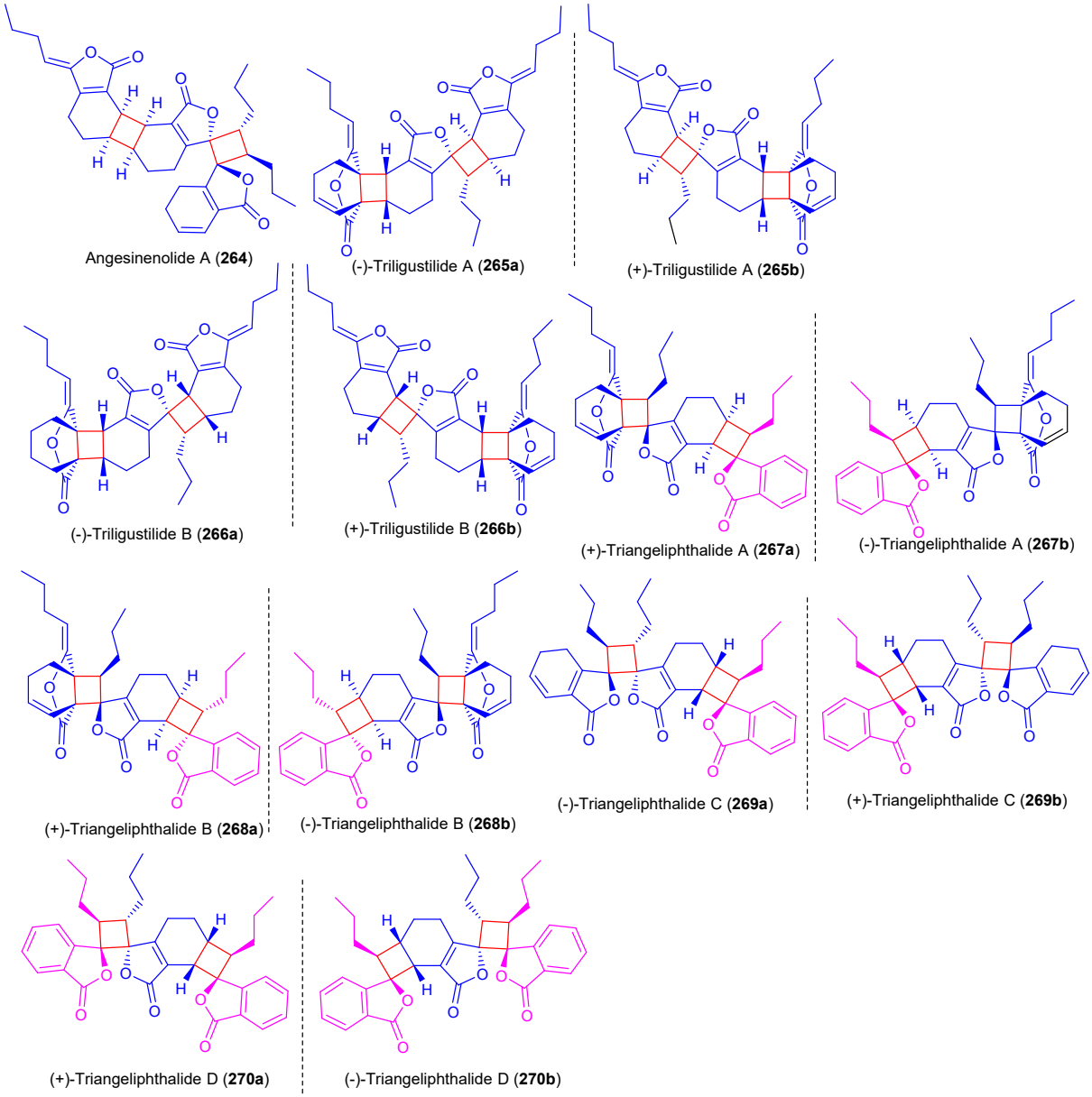
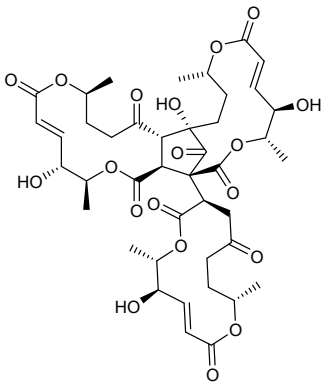
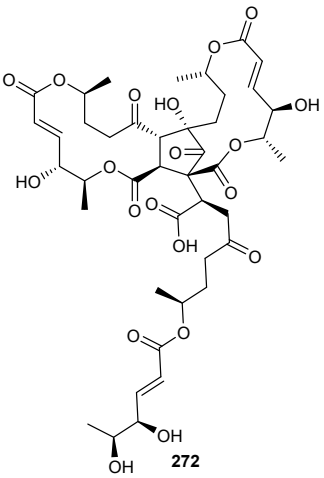


Table S15 Structure names, sources and bioactivity of trimers **264-270**.

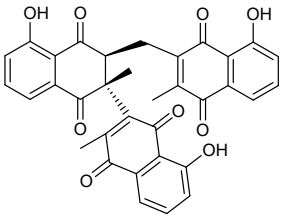
No	Compound	Sources	Bioactivity
264	Angesinine A	*Angelica sinensis*[61]	Anticoagulant[61]
265	Triligustilide A	*Angelica sinensis*[62]	Anti-inflammatory[62]
266	Triligustilide B	*Angelica sinensis*[62]	Anti-inflammatory[62]
267	Triangeliphthalide A	*Angelica sinensis*[63]	
268	Triangeliphthalide B	*Angelica sinensis*[63]	
269	Triangeliphthalide C	*Angelica sinensis*[63]	Anti-inflammatory[63]
270	Triangeliphthalide D	*Angelica sinensis*[63]	Anti-inflammatory[63]



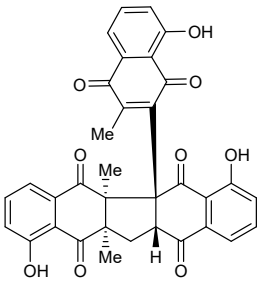
271



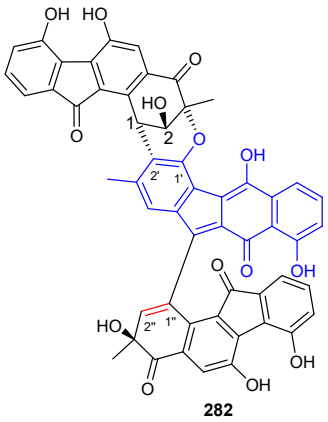
272



revised structure
Plumbazeylanone (**281**)



original structure
Plumbazeylanone (**278**)



282

Table S16 Structure names, sources and bioactivity of trimers **271-272,** and **281-282**.

No	Compound	Sources	Bioactivity
271	Acaulin A	*Acaulium* sp.[64]	Antiosteoporotic[64]
272	Acaulin B	*Acaulium* sp.[64]	Antiosteoporotic[64]
281	Plumbazeylanone	*Plumbago zeylanica*[65]	
282	Trifluostatin A	*Streptomyces albus*[66]	

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