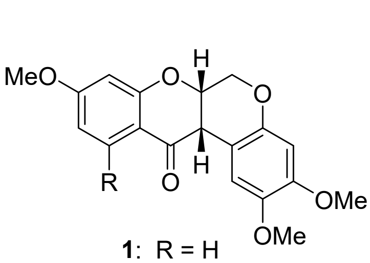
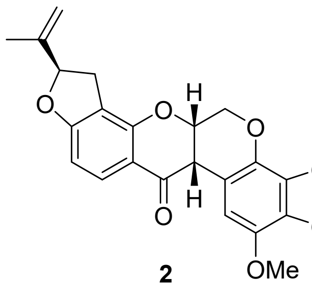
Rotenoid diversity, distribution and evolution in plant lineages

Vaderament-A. Nchiozem-Ngnitedem,*[a] Alan Paton [b] and Gabin Thierry M. Bitchagno*[b]



1: R = H
3: R = OH



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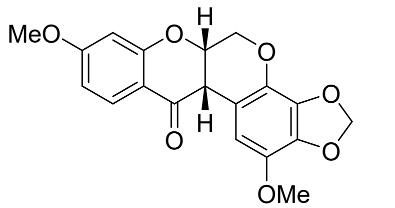

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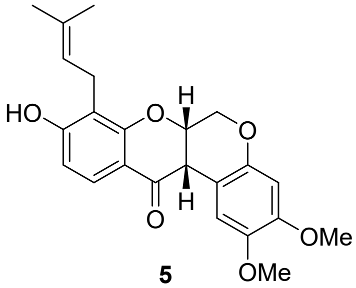

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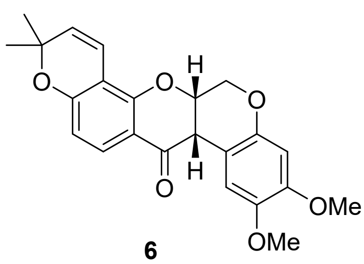

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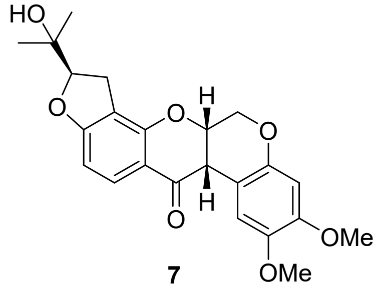

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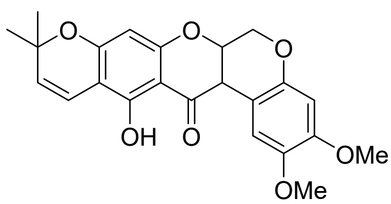

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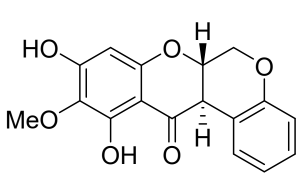

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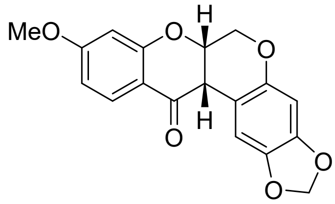

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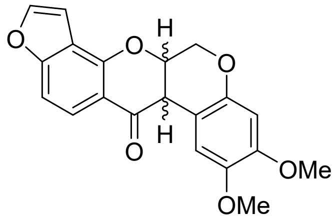

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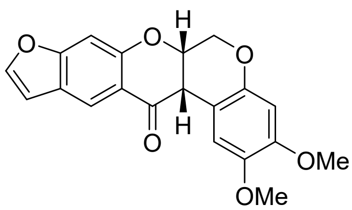

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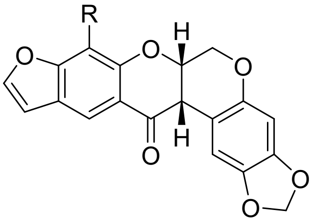
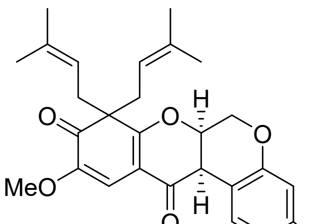


51: R = H
52: R = OMe



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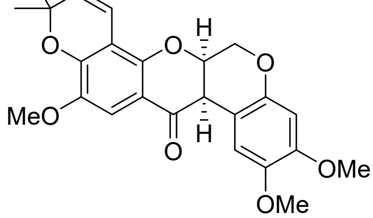

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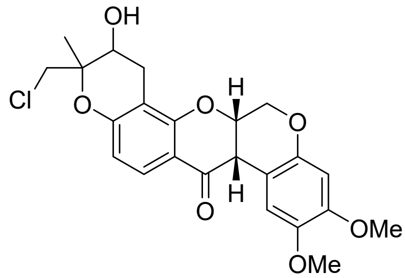

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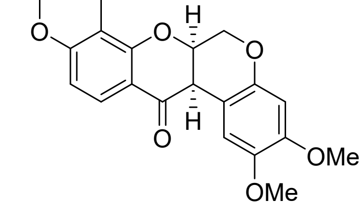

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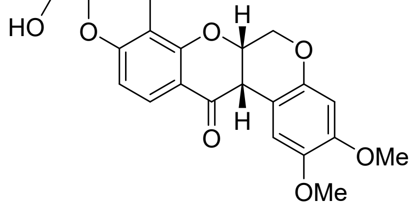

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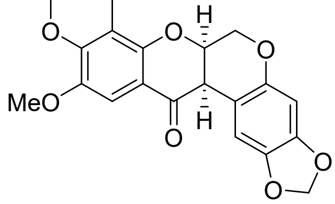

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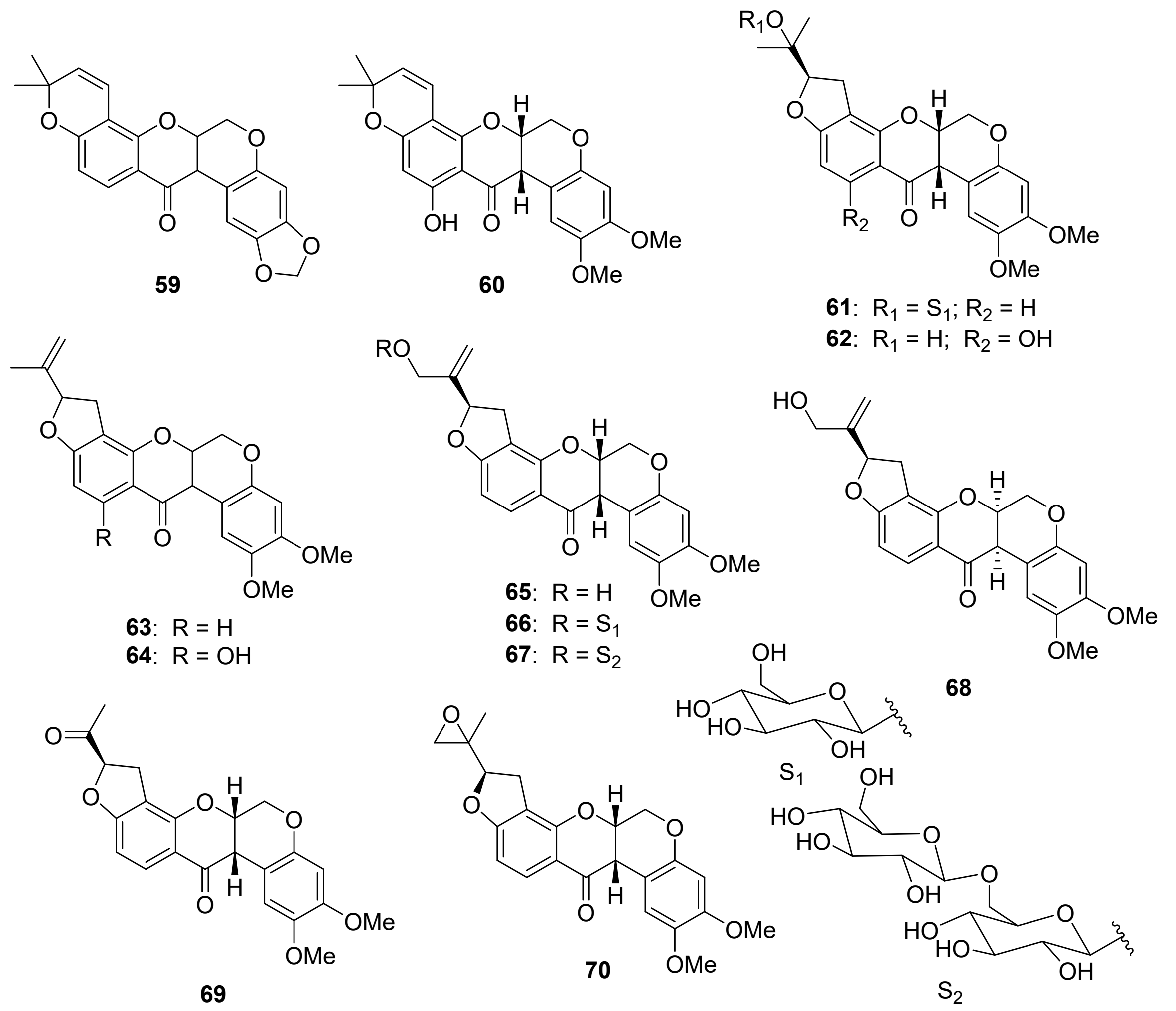
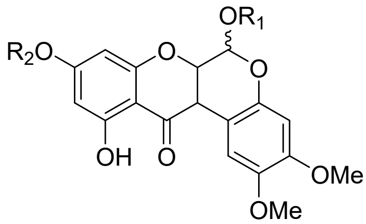
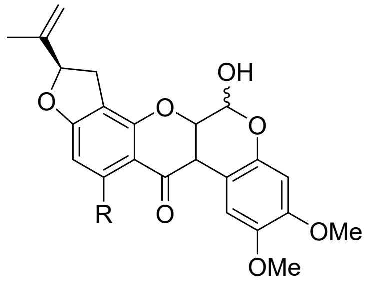


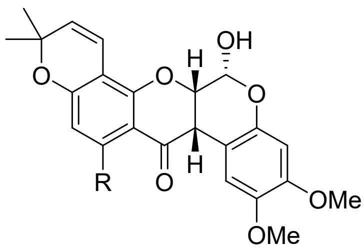
Figure S1. Rotenoids sensu stricto with an unmodified backbone (**Type I**) : munduserone (**1**),[1] piscicartone (**2**),[2] sermundone (**3**),[3,4] oblarotenoid E (**4**),[5] rot-2′-enonic acid (**5**),[6] deguelin (**6**),[7] dalpanol (**7**),[8] 12a-hydroxy-β-toxicarol (**8**),[9] crocetenone (**9**),[10] oblarotenoid C (**48**),[11] elliptone (**49**),[12] erosone (**50**),[13,14] dolineone (**51**),[14] pachyrrhizone (**52**),[14] caeruleanone A (**53**),[15] (+)-erythynone (**54**),[16] 7′-chloro-5′-hydroxy-4′,5′-dihydrodeguelin (**55**),[17] derrisin (**56**),[18] 7′-hydroxydeguelin (**57**),[19] (−)-3-deoxycaeruleanone D (**58**),[20] millettone (**59**),[21] *α*-toxicarol (**60**),[3] 6'-O-β-D-glucopyranosyldalpanol (**61**),[22] 11-hydroxydalpanol (**62**),[8] rotenone (**63**),[7] sumatrol (**64**),[7] amorphigenin (**65**),[22] (8′-O-β-D-glucopyranosyl-amorphigenin (**66**), amorphin (**67**)),[23] (6aR,12aR,5′R)-amorphigenin (**68**),[6] (7′-*nor*-6′-oxo-2′,3′-dehydrorotenone (**69**), (6′*S*)-6′,7′-epoxyrotenone (**70**)).[19]



10: R_1 = H; R_2 = CH_3
71: R_1 = H; R_2 = H
72: R_1 = Ac; R_2 = CH_3

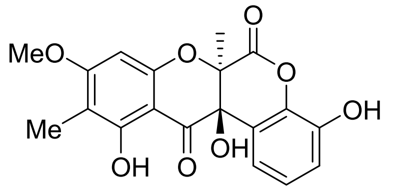


11: R = OH
73: R = H



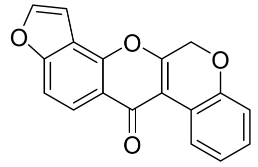
74: R = H
75: R = OH

Figure S2. 6-Hydroxyrotenoid (**Type II**) : dihydrostemonal (**10**),[1] villosin (**11**),[7] 9-demethyldihydrostemonal (**71**),[1] 6-acetoxydihydrostemonal **(72)**,[1] 6-hydroxyrotenone (**73**),[7] (–)-13α-hydroxydeguelin (**74**),[24] 6α-hydroxy-α-toxicarol (**75**).[25]



12

Figure S3. 6-Ketorotenoids (**Type III**): mirabijalone S (**12**).[26]



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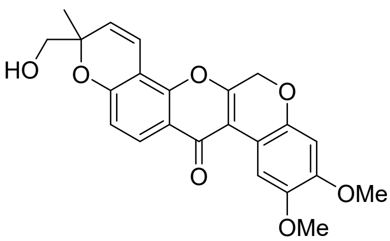

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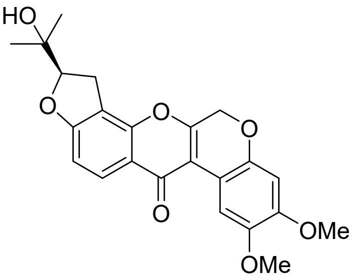

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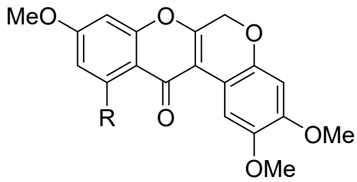
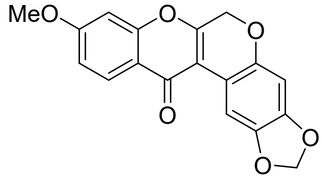


76: R = OH
77: R = H



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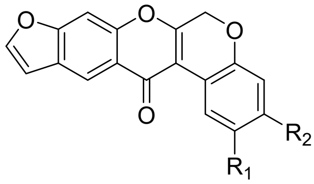
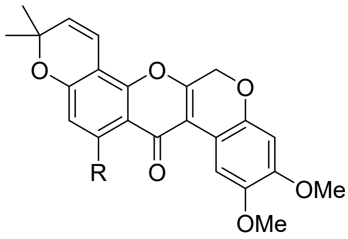
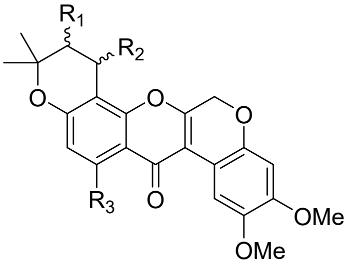


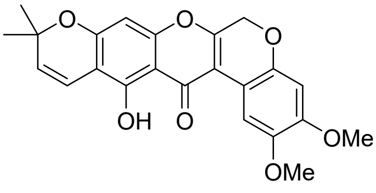
79: R_1 = R_2 = OCH_2O
80: R_1 = R_2 = OMe



81: R = H
82: R = OH



83: R_1 = αOH; R_2 = αOMe; R_3 = OH
84: R_1 = βOH; R_2 = βOH; R_3 = H
85: R_1 = αOH; R_2 = αOH; R_3 = OH



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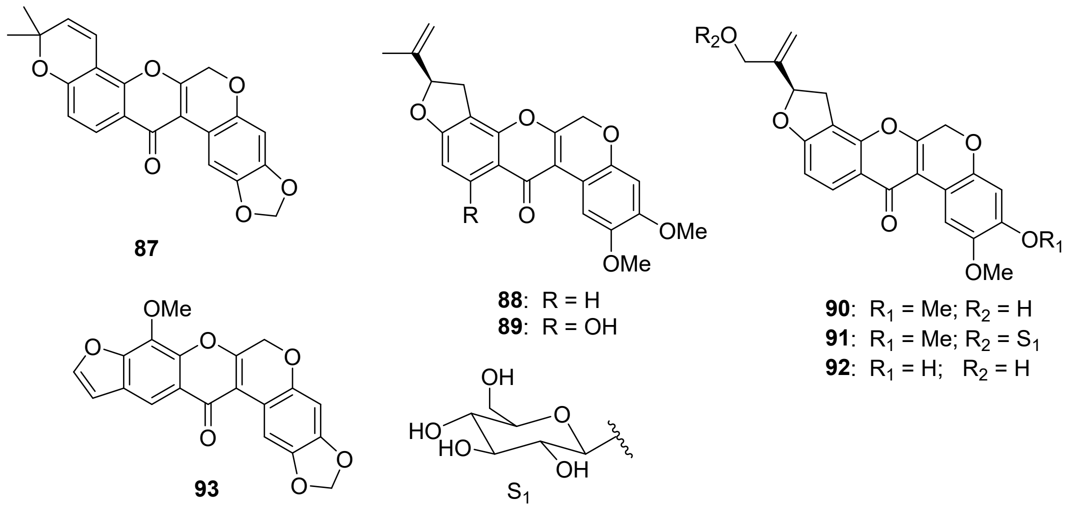
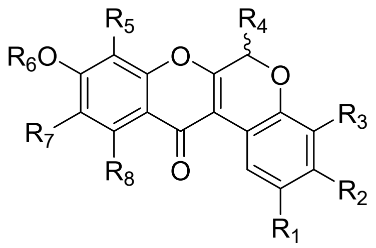
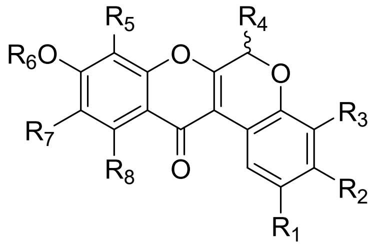


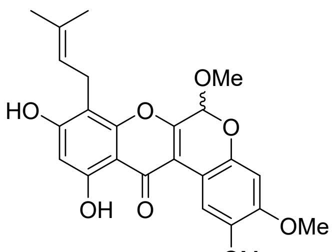
Figure S4. Dehydrorotenoids with an unmodified backbone (**Type IV**): pongarotene (**13**),[27] 7′-hydroxy-6a,12a-dehydrodeguelin (**14**),[28] 6′-hydroxy-6a,12a-dehydrorotenone (**15**),[28] 6a,12a-dehydrosermundone (**76**),[3] dehydromunduserone (**77**),[29] 9-methoxy-2,3-methylenedioxy-6a,2a-dehydrorotenoid (**78**),[5] dehydrodolineone (**79**),[14] dehydroisoelliptone (**80**),[14] 6a,12a-dehydrodeguelin (**81**),[30] 6a,12a-dehydro-α-toxicarol (**82**),[31] 4,5-dihydro-5′α-hydroxy-4′α-methoxy-6a,12a-dehydro-α-toxicarol (**83**),[32] (4′,5′-dihydroxy-6a,12a-dehydrodeguelin (**84**), 11,4′,5′-trihydro-6a,12a-dehydrodeguelin (**85**)),[33] 6a,12a-dehydro-β-toxicarol (**86**),[9] 6a,12a-dehydromillettone (**87**),[34,35] dehydrorotenone (**88**),[18] villosol (**89**),[36] dehydroamorphigenin (**90**),[37] 6a,12a-didehydroamorphigen glucoside (**91**),[38] 6a,12a-dehydro-3-*O*-demethylamorphigenin (**92**),[6] dehydroypachyrrhizone (**93**).[14]



16: R_1 = H; R_2 = H; R_3 = OH; R_4 = OH; R_5 = H; R_6 = Me; R_7 = H; R_8 = OH
17: R_1 = H; R_2 = H; R_3 = H; R_4 = OH; R_5 = OMe; R_6 = H; R_7 = H; R_8 = OH
19: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = αOH; R_5 = H; R_6 = Me; R_7 = H; R_8 = OGlc
20: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = H; R_6 = Me; R_7 = H; R_8 = OH
21: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OEt; R_5 = H; R_6 = Me; R_7 = H; R_8 = OH
22: R_1 = H; R_2 = H; R_3 = H; R_4 = OMe; R_5 = H; R_6 = H; R_7 = Me; R_8 = OH
94: R_1 = H; R_2 = H; R_3 = H; R_4 = OH; R_5 = H; R_6 = H; R_7 = Me; R_8 = OH
95: R_1 = H; R_2 = H; R_3 = OH; R_4 = OH; R_5 = H; R_6 = H; R_7 = H; R_8 = OH
96: R_1 = H; R_2 = H; R_3 = H; R_4 = OAc; R_5 = H; R_6 = H; R_7 = OH; R_8 = OH
97: R_1 = H; R_2 = OH; R_3 = H; R_4 = OAc; R_5 = H; R_6 = H; R_7 = OH; R_8 = OH
98: R_1 = H; R_2 = OH; R_3 = H; R_4 = OMe; R_5 = H; R_6 = H; R_7 = Me; R_8 = OH
99: R_1 = H; R_2 = OH; R_3 = H; R_4 = OH; R_5 = H; R_6 = H; R_7 = Me; R_8 = OH



100: R_1 = H; R_2 = H; R_3 = H; R_4 = OH; R_5 = H; R_6 = H; R_7 = H; R_8 = OH
101: R_1 = H; R_2 = H; R_3 = OH; R_4 = $OCO(CH_2)_3CH_3$; R_5 = H; R_6 = H; R_7 = Me; R_8 = H
102: R_1 = H; R_2 = H; R_3 = OH; R_4 = OH; R_5 = H; R_6 = Me; R_7 = Me; R_8 = OH
103: R_1 = H; R_2 = H; R_3 = OH; R_4 = OH; R_5 = Me; R_6 = H; R_7 = Me; R_8 = OH
104: R_1 = H; R_2 = OH; R_3 = H; R_4 = OH; R_5 = H; R_6 = Me; R_7 = Me; R_8 = OH
105: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = H; R_6 = Me; R_7 = H; R_8 = H
106: R_1 = H; R_2 = OH; R_3 = H; R_4 = OMe; R_5 = H; R_6 = H; R_7 = Me; R_8 = OH
107: R_1 = H; R_2 = H; R_3 = OH; R_4 = OMe; R_5 = H; R_6 = Me; R_7 = H; R_8 = OH
108: R_1 = H; R_2 = H; R_3 = OH; R_4 = OMe; R_5 = H; R_6 = Me; R_7 = Me; R_8 = OH
109: R_1 = H; R_2 = H; R_3 = H; R_4 = OH; R_5 = H; R_6 = Me; R_7 = OH; R_8 = OH
110: R_1 = H; R_2 = H; R_3 = H; R_4 = OH; R_5 = OH; R_6 = Me; R_7 = Me; R_8 = OH
111: R_1 = H; R_2 = H; R_3 = H; R_4 = OMe; R_5 = H; R_6 = H; R_7 = H; R_8 = OH
112: R_1 = H; R_2 = H; R_3 = H; R_4 = OMe; R_5 = OMe; R_6 = H; R_7 = Me; R_8 = OH
113: R_1 = H; R_2 = H; R_3 = H; R_4 = OH; R_5 = OMe; R_6 = H; R_7 = Me; R_8 = OH
114: R_1 = H; R_2 = OH; R_3 = H; R_4 = OH; R_5 = H; R_6 = H; R_7 = H; R_8 = OH
115: R_1 = H; R_2 = H; R_3 = H; R_4 = OMe; R_5 = H; R_6 = H; R_7 = OMe; R_8 = OH
116: R_1 = H; R_2 = H; R_3 = H; R_4 = OMe; R_5 = H; R_6 = Me; R_7 = Me; R_8 = OH
117: R_1 = H; R_2 = H; R_3 = H; R_4 = αOMe; R_5 = H; R_6 = H; R_7 = H; R_8 = OMe
118: R_1 = H; R_2 = H; R_3 = H; R_4 = αOMe; R_5 = H; R_6 = H; R_7 = Me; R_8 = OMe
119: R_1 = H; R_2 = H; R_3 = OH; R_4 = OH; R_5 = OMe; R_6 = Me; R_7 = Me; R_8 = OH
120: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = αOMe; R_5 = H; R_6 = Me; R_7 = H; R_8 = OGlc
121: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = αOMe; R_5 = H; R_6 = Me; R_7 = H; R_8 = OH



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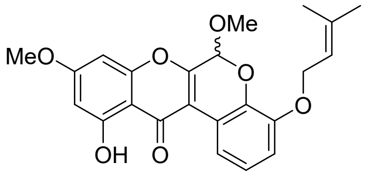

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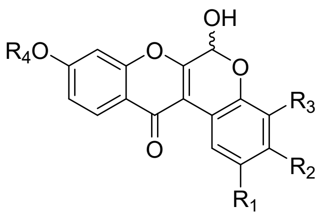
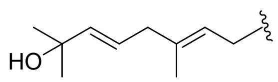
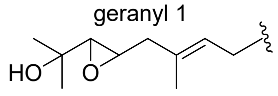


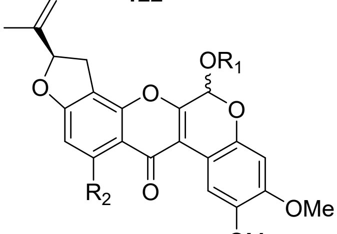
18: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = geranyl 1
124: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = geranyl 2
125: R_1 = R_2 = OCH_2O; R_3 = OMe; R_4 = geranyl 1



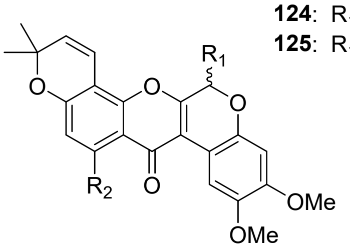
geranyl 1



geranyl 2

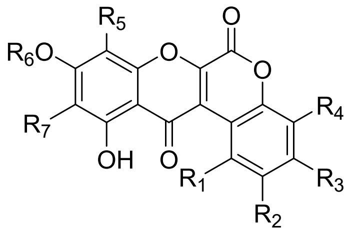


126: R_1 = H; R_2 = H
127: R_1 = Me; R_2 = OH
128: R_1 = H; R_2 = OH

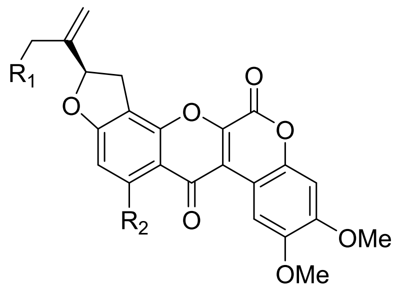


129: R_1 = OMe; R_2 = H
130: R_1 = OH; R_2 = H
131: R_1 = OH; R_2 = OH
132: R_1 = αOH; R_2 = OH

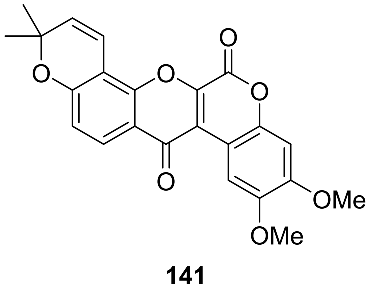
Figure S5. 6-Hydroxydehydroxyrotenoid (**Type V**): boeravinone O (**16**),[39] berectone A (**17**),[40] stuhlmarotenoid A (**18**),[41] stemonal 11-O-β-D-glucopyranoside (**19**),[42] stemonal (**20**),[43] stemonacetal (**21**),[44] (boeravinones A (**22**), and B (**94**)),[45] boerharotenoid B (**95**),[46] (repenone (**96**), repenol (**97**)),[47] (boeravinone D (**98**),[48] boeravinone E (**99**)),[49] coccineone B (**100**),[50] diffusarotenoid (**101**),[51] 9-*O*-methyl-4-hydroxyboeravinone B (**102**),[52] (mirabijalones B (**103**), and D (**104**)),[53] 6-hydroxy-2,3,9-trimethoxy-[1]-benzopyrano[3,4-*b*][1]benzopyran-12(6*H*)-one (**105**),[54] (boeravinone D (**106**), boeravinone G (**107**), boeravinone H (**108**)),[55] 9-*O*-methyl-10-hydroxycoccineone B (**109**),[56] boeravinone I (**110**),[57] (boeravinones K-N (**111-114**)),[39] boeravinone P (**115**),[48] boeravinone A methyl ether (**116**),[58] (6R,11-dimethoxy-9-hydroxyrotenoid (**117**), 6R,11-dimethoxy-9-hydroxy-10-methylrotenoid (**118**)),[48] berectone B (**119**),[40] (6-O-methylstemonal 11-O-β-D-glucopyranoside (**120**), 6-O-stemonal (**121**)),[42] 6a,12a-dehydro-2,3,6-trimethoxy-8-(3',3'-dimethylallyl)-9,11-dihydroxyrotenone (**122**),[59] boeractanone (**123**),[60] (stuhlmarotenoids B (**124**), and C (**125**)),[41] amorpholone (**126**),[61] villinol (**127**),[36] 12a-dehydro-6-hydroxysumatrol (**128**),[62] (6-methoxy-6a,12a-dehydrodeguelin (**129**), 6-hydroxy-6a,12a-dehydrodeguelin (**130**)),[12] 6-hydroxy-6a,12a-dehydro-α-toxicarol (**131**),[3] (−)-6-hydroxy-6a,12a-dehydro-α-toxicarol (**132**).[63]



23: R_1 = H; R_2 = OMe; R_3 = OMe; R_4 = H; R_5 = H; R_6 = Me; R_7 = H
24: R_1 = H; R_2 = H; R_3 = OH; R_4 = H; R_5 = H; R_6 = H; R_7 = Me
133: R_1 = H; R_2 = H; R_3 = H; R_4 = H; R_5 = H; R_6 = H; R_7 = Me
134: R_1 = H; R_2 = H; R_3 = H; R_4 = OH; R_5 = H; R_6 = H; R_7 = Me
135: R_1 = H; R_2 = H; R_3 = OMe; R_4 = OH; R_5 = H; R_6 = Me; R_7 = Me
136: R_1 = H; R_2 = H; R_3 = H; R_4 = OH; R_5 = Me; R_6 = H; R_7 = Me
137: R_1 = OH; R_2 = H; R_3 = H; R_4 = H; R_5 = Me; R_6 = H; R_7 = Me

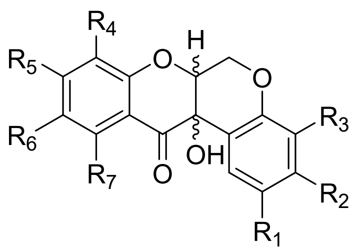


138: R_1 = H; R_2 = H
139: R_1 = H; R_2 = OH
140: R_1 = OH; R_2 = H

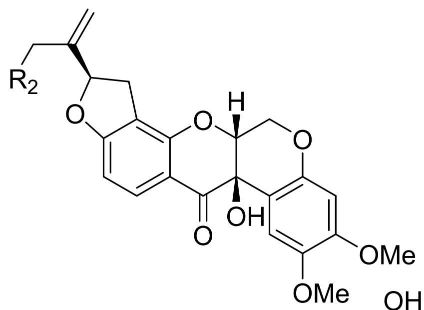


141

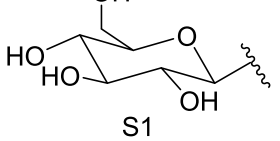
Figure S6. 6-Ketodehydroxyrotenoid (**Type VI**): stemonone (**23**),[64] boeravinone F (**24**),[46] mirabijalone E (**133**),[48] (mirabijalones T-W (**134-137**)),[26] rotenonone (**138**),[17] villosone (**139**),[36] 6-ketodehydroamotphigenin (**140**),[65] 6-*oxo*-6a,12a-dehydrodeguelin (**141**),[12]



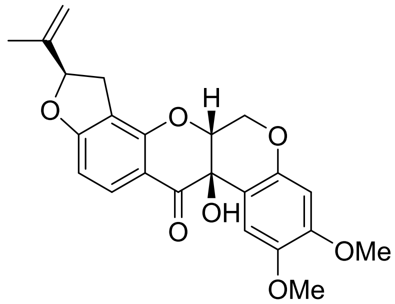
25: $R_1 = R_2 = OCH_2O$; $R_3 = H$; $R_4 = R_5 = OCH_2O$; $R_6 = H$; $R_7 = H$; (6aβ,12aα)
26: $R_1 = H$; $R_2 = H$; $R_3 = OH$; $R_4 = H$; $R_5 = OMe$; $R_6 = Me$; $R_7 = OH$; (6aα,12aβ)
27: $R_1 = H$; $R_2 = H$; $R_3 = H$; $R_4 = H$; $R_5 = OH$; $R_6 = OMe$; $R_7 = OH$; (6aβ,12aα)
28: $R_1 = OMe$; $R_2 = OMe$; ; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = OGlc$; (6aβ,12aβ)
33: $R_1 = OMe$; $R_2 = OMe$; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = OH$; (6aβ,12aβ)
34: $R_1 = OMe$; $R_2 = OMe$; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = OH$; (6aα,12aα)
142: $R_1 = OMe$; $R_2 = OMe$; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = H$; (6aβ,12aβ)
143: $R_1 = R_2 = OCH_2O$; $R_3 = H$; $R_4 = OMe$; $R_5 = OMe$; $R_6 = H$; $R_7 = H$; (6aβ,12aα)
144: $R_1 = H$; $R_2 = H$; ; $R_3 = OH$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = OH$; (6aα,12aβ)
145: $R_1 = H$; $R_2 = H$; ; $R_3 = OH$; $R_4 = H$; $R_5 = OH$; $R_6 = H$; $R_7 = OH$; (6aα,12aβ)
146: $R_1 = H$; $R_2 = H$; ; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = OMe$; $R_7 = OH$; (6aα,12aβ)
147: $R_1 = H$; $R_2 = H$; ; $R_3 = OH$; $R_4 = H$; $R_5 = OMe$; $R_6 = Me$; $R_7 = OH$; (6aα,12aβ)
148: $R_1 = H$; $R_2 = OMe$; ; $R_3 = H$; $R_4 = H$; $R_5 = OH$; $R_6 = H$; $R_7 = H$; (6aβ,12aβ)
149: $R_1 = OMe$; $R_2 = OMe$; ; $R_3 = H$; $R_4 = H$; $R_5 = OH$; $R_6 = H$; $R_7 = H$; (6aβ,12aβ)
150: $R_1 = H$; $R_2 = H$; ; $R_3 = OH$; $R_4 = Me$; $R_5 = OMe$; $R_6 = Me$; $R_7 = OH$
151: $R_1 = H$; $R_2 = H$; ; $R_3 = OH$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = OH$; (6aβ,12aα)
152: $R_1 = H$; $R_2 = H$; ; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = Me$; $R_7 = OH$; (6aα,12aβ)
153: $R_1 = H$; $R_2 = H$; ; $R_3 = H$; $R_4 = OMe$; $R_5 = OMe$; $R_6 = H$; $R_7 = OH$; (6aα,12aβ)
154: $R_1 = H$; $R_2 = H$; ; $R_3 = OH$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = OGlc$; (6aα,12aβ)
155: $R_1 = H$; $R_2 = H$; ; $R_3 = OMe$; $R_4 = H$; $R_5 = OMe$; $R_6 = Me$; $R_7 = OH$; (6aα,12aβ)
156: $R_1 = R_2 = OCH_2O$; $R_3 = H$; $R_4 = H$; $R_5 = OCH_3$; $R_6 = OCH_3$; $R_7 = H$; (6aβ,12aβ)
157: $R_1 = R_2 = OCH_2O$; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = H$; (6aβ,12aβ)
158: $R_1 = R_2 = OCH_2O$; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = H$; (6aβ,12aα)
159: $R_1 = OMe$; $R_2 = R_3 = OCH_2O$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = H$; (6aβ,12aβ)
160: $R_1 = H$; $R_2 = H$; ; $R_3 = OH$; $R_4 = OMe$; $R_5 = OH$; $R_6 = Me$; $R_7 = OH$; (6aα,12aβ)
161: $R_1 = OMe$; $R_2 = OMe$; $R_3 = H$; $R_4 = H$; $R_5 = OH$; $R_6 = H$; $R_7 = OH$; (6aα,12aα)
162: $R_1 = OH$; $R_2 = OMe$; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = OH$; (6aα,12aα)
163: $R_1 = OMe$; $R_2 = OH$; $R_3 = H$; $R_4 = H$; $R_5 = OMe$; $R_6 = H$; $R_7 = OH$; (6aα,12aα)



29: $R = OS_1$



S1



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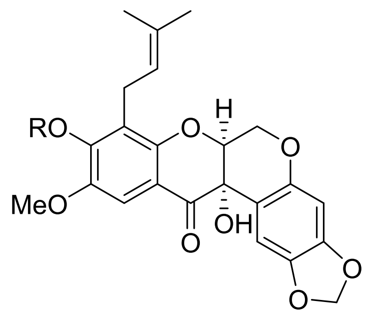
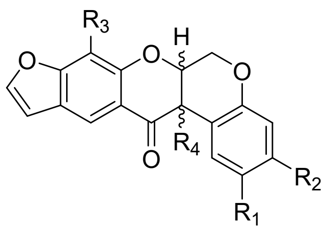
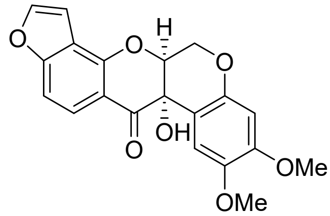


31: R = prenyl
32: R = H



164: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OMe
165: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; (6aβ,12aβ)
166: R_1 = R_2 = OCH_2O; R_3 = H; R_4 = OH; (6aβ,12aβ)
167: R_1 = R_2 = OCH_2O; R_3 = OMe; R_4 = OH; (6aβ,12aβ)



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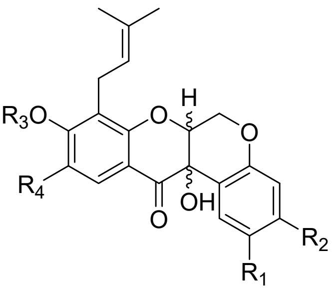
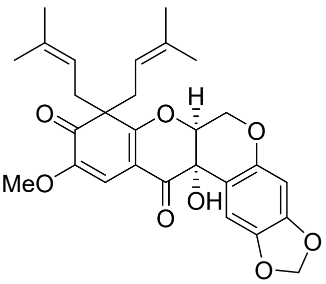


169: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = H; (6aβ,12aβ)
170: R_1 = R_2 = OCH_2O; R_3 = Me; R_4 = H; (6aβ,12aα)
171: R_1 = OMe; R_2 = OMe; R_3 = Glc; R_4 = H



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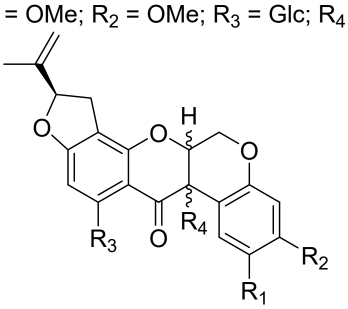
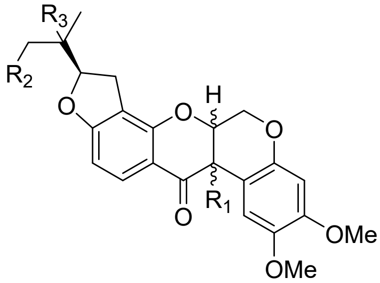
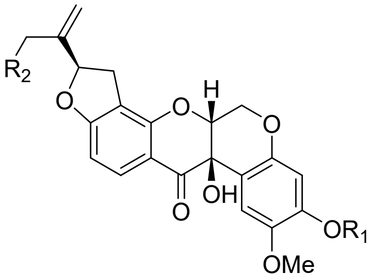


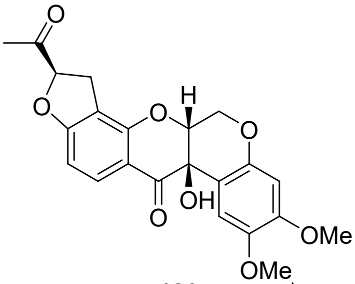
173: R_1 = R_2 = OCH_2O; R_3 = H; R_4 = OH; (6aβ,12aβ)
174: R_1 = OMe; R_2 = OMe; R_3 = OH; R_4 = OH
175: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OMe; (6aβ,12aβ)
176: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; (6aβ,12aα)
177: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OMe; (6aβ,12aα)



178: R_1 = OH; R_2 = H; R_3 = OH; (6aβ,12aβ)
179: R_1 = OH; R_2 = H; R_3 = OH
180: R_1 = OH; R_2 = H; R_3 = OGlc
181: R_1 = OH; R_2 = OGlc; R_3 = OH; (6aβ,12aβ)
182: R_1 = OH; R_2 = OH; R_3 = OGlc; (6aβ,12aβ)



183: R_1 = Me; R_2 = OH
184: R_1 = Me; R_2 = OS_2
185: R_1 = H; R_2 = OH



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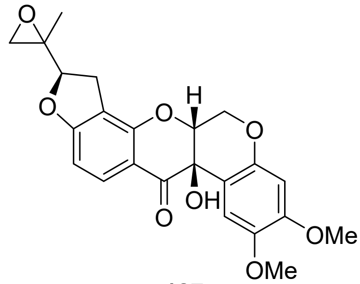

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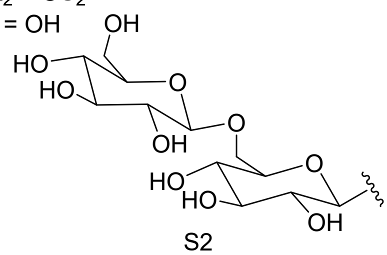
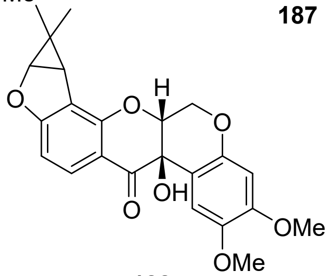


S2



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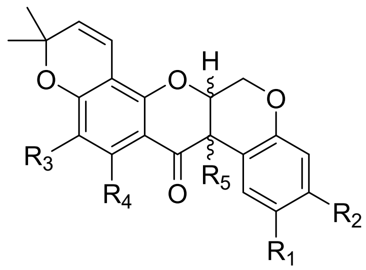
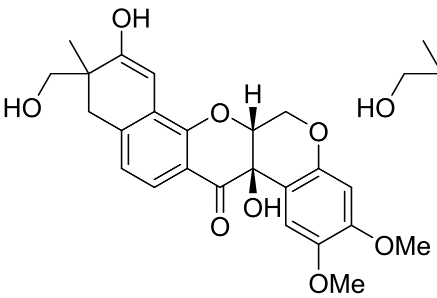


189: R_1 = OMe; R_2 = OMe; R_3 = OMe; R_4 = H; R_5 = OH; (6aα, 12aα)
190: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = OH; (6aβ, 12aβ)
191: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = OH
192: R_1 = R_2 = OCH_2O; R_3 = H; R_4 = H; R_5 = OH; (6aβ, 12aα)
193: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = H; R_5 = OH; (6aβ, 12aα)
194: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = H; R_5 = OMe; (6aβ, 12aα)
195: R_1 = R_2 = OCH_2O; R_3 = H; R_4 = H; R_5 = OH; (6aβ, 12aβ)
196: R_1 = R_2 = OCH_2O; R_3 = OMe; R_4 = H; R_5 = OH; (6aα, 12aα)
197: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = OH; (6aβ, 12aβ)
198: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = OH; (6aα, 12aα)
199: R_1 = OH; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = OH; (6aα, 12aα)



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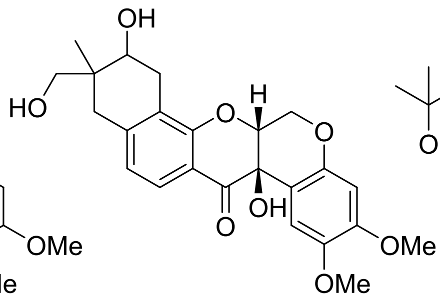

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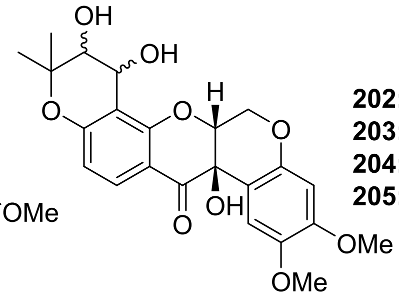
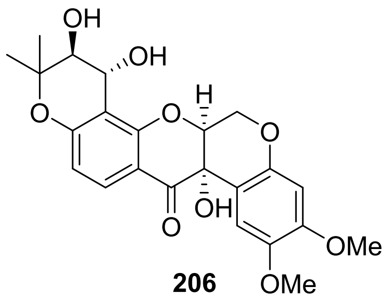


202: 4'β, 5'β
203: 4'β, 5'α
204: 4'α, 5'α
205: 4'β, 5'β



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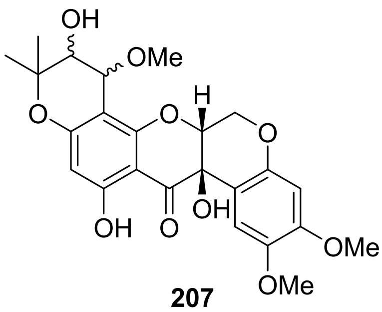

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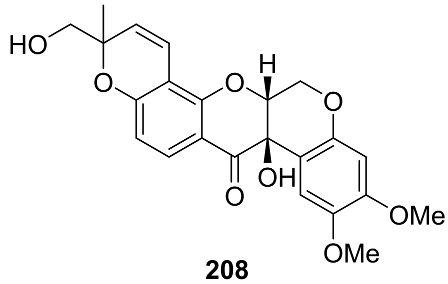
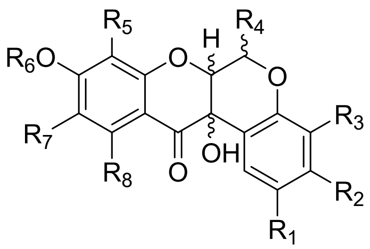
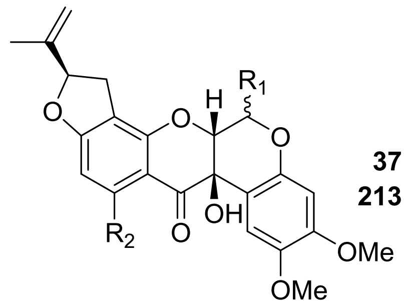


208

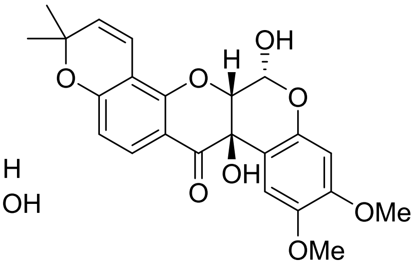
Figure S7. 12a-Hydroxyrotenoids with an unmodified backbone (**Type VII**): (+)-usararotenoid-A (**25**),[35] boeravinone C (**26**),[66] irispurinol (**27**),[67] 6-deoxyclitoriacetal 11-O-β-D-glucopyranoside (**28**),[68] dalbin (**29**),[23] (–)-3-hydroxyrotenone (**30**),[16,20] (caeruleanones B (**31**) and C (**32**)),[15] (+)-6-deoxyclitoriacetal (**33**),[3] (–)-(6aS,12aS)-6-deoxyclitoriacetal (**34**),[4] 12a-hydroxymunduserone (**142**),[14] (+)-usararotenoid-B (**143**),[69] (coccineones C (**144**), D (**145**), and E (**146**)),[70] boerhavone C (**147**),[70] (gliricidol (**148**), 2-methoxygliricidol (**149**)),[71] mirabijalone A (**150**),[53] 10-demethylboeravinone C (**151**),[56] abronione (**152**),[72] (8-methoxy-10-demethoxycoccineone E (**153**), 10-demethylboeravinone C 11-O-β-D-glucopyranoside (**154**)),[66] abronione A (**155**),[58] (6aR,12aR)-9,10-dimethoxy-2,3-methylenedioxyrotenoid (**156**),[5] (oblarotenoid A (**157**), oblarotenoid B (**158**), oblarotenoid D (**159**)),[5,11] berectone C (**160**),[73] ((–)-(6a*S*,12a*S*)-millettiabrandisin A (**161**), (–)-(6a*S*,12a*S*)-millettiabrandisin B (**162**), (–)-(6a*S*,12a*S*)-millettiabrandisin C (**163**),[4] neobanone (**164**),[74] 12a-hydroxyerosone (**165**),[13] (12a-hydroxydolineone (**166**), 12a-hydroxypachyrrhizone (**167**)),[75] 6aα,12aα-12a-hydroxyelliptone (**168**),[76] 12aβ-hydroxyrot-2′-enonic acid (**169**),[17] usararotenoid C (**170**),[35] *O*-β-D-glucopyranolsyl-12αβ-hydroxyro-2′-enoic acid (**171**),[38] (−)-3-hydroxycaeruleanone A (**172**),[20] 12a-hydroxyisomilletone (**173**),[14] villosinol (**174**),[16,20] (12aβ-methoxyrotenone (**175**), 12aα-hydroxyrotenone (**176**)),[17] 12aα-methoxyrotenone (**177**),[77] 12a-hydroxydalpanol (**178**),[22] 12α-hydroxydalpanol (**179**),[8] 6′-O-β-D-glucopyranosyl-12a-hydroxydalpanol (**180**),[78] (amorphasides B (**181**), and C (**182**)),[23] 12a-hydroxyamorphigenin (**183**),[22] amorphaside D (**184**),[23] 3-*O*-demethyldalbinol (**185**),[6] (7′-*nor*-6′-*oxo*-4′,5′-dehydrorotenolone (**186**),[17] (6′*R*)-6′,7′-epoxy-12aβ-hydroxyrotenone (**187**)),[19] sarcolobin (**188**),[79] (+)-12a-hydroxyerythynone (**189**),[16] 11-hydroxytephrosin (**190**),[20] 12a-hydroxy-α-toxicarol (**191**),[80] (+)-12a-epimillettosin (**192**),[69] (12aα-hydroxydeguelin (**193**), 12aα-methoxydeguelin (**194**)),[77] (–)-milletosin (**195**),[81] (−)-caeruleanone D (**196**),[20] ((−)-(6a*R*,12a*R*)-12a-hydroxy-α-toxicarol (**197**),[4] ((+)-(6a*R*,12a*R*)-12a-hydroxy-α-toxicarol (**198**), (+)-(6a*R*,12a*R*)-millettiapachycarpin (**199**)),[63] ((5′,7′-dihydroxytephrosin (**200**), 4′,5′-dihydro-5′,7′-dihydroxytephrosin (**201**)),[17] (6aR,12aR,4′R,5′S)-4′,5′-dihydro-4′,5′-dihydroxytephrosin (**202**),[28] ((6aR,12aR,4′S,5′R)-4′,5′-dihydro-4′,5′-dihydroxytephrosin (**203**), (6aR,12aR,4′R,5′R)-4′,5′-dihydro-4′,5′-dihydroxytephrosin (**204**), (6aR,12aR,4′S,5′S)-4′,5′-dihydro-4′,5′-dihydroxytephrosin (**205**)),[17] *trans*-4′,5′-dihydro-12aβ-4′β,5′α-trihydroxydeguelin (**206**),[18] 4′,5′-dihydro-11,5′-dihydroxy-4′-methoxytephrosin (**207**),[82] 7′-hydroxytephrosin (**208**).[19]



35: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = H; R_6 = Me; R_7 = H; R_8 = OH; (6aβ,12aβ)
36: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = αOH; R_5 = H; R_6 = Me; R_7 = H; R_8 = OGlc;(6aβ, 12aβ)
38: R_1 = H; R_2 = H; R_3 = OH; R_4 = βOMe; R_5 = H; R_6 = Me; R_7 = Me; R_8 = OH; (6aβ,12aα)
209: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = OH; R_5 = H; R_6 = Me; R_7 = H; R_8 = H; (6aβ,12aβ)
210: R_1 = OMe; R_2 = OMe; R_3 = H; R_4 = αOH; R_5 = H; R_6 = H; R_7 = H; R_8 = OH; (6aβ,12aβ)
211: R_1 = H; R_2 = H; R_3 = OH; R_4 = αOMe; R_5 = Me; R_6 = Me; R_7 = Me; R_8 = OH; (6aα,12aβ)
212: R_1 = H; R_2 = H; R_3 = OMe; R_4 = αOMe; R_5 = H; R_6 = Me; R_7 = Me; R_8 = OH; (6aα,12aβ)

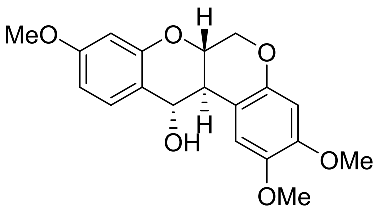


37: R_1 = αOGlc; R_2 = H
213: R_1 = βOH; R_2 = OH



214

Figure S8. 6,12a-Dihydroxyrotenoids (**Type VIII**): clitoriacetal (**35**),[44] clitoriacetal 11-O-β-D-glucopyranoside (**36**),[83] amorphaside A (**37**),[23] 6-methoxyboeravinone C (**38**),[52] (11-deoxyclitoriacetal (**209**), 9-demethylclitoriacetal (**210**)),[43] ~~6-demethylboeravinone G~~ (**201**),[66] (multiferones A (**211**), and B (**212**)),[84] villol (**213**),[36] (–)-13α-hydroxytephrosin (**214**).[24]



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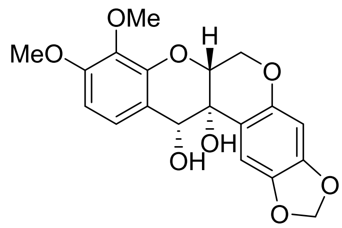

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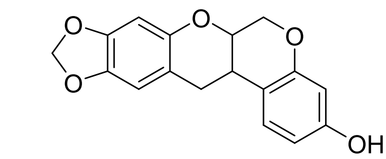

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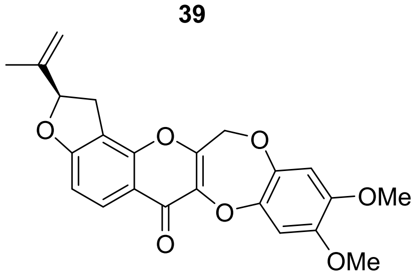

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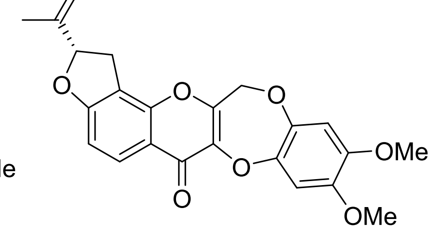

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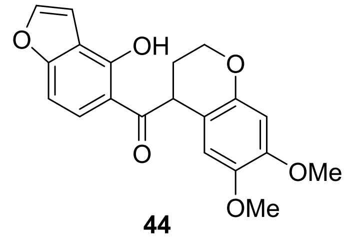

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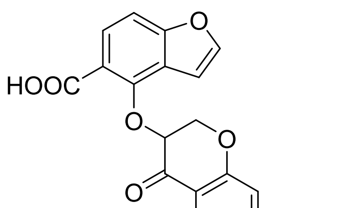

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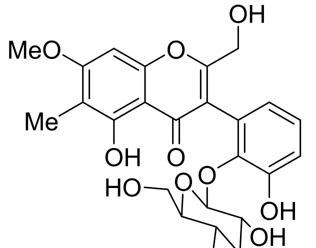
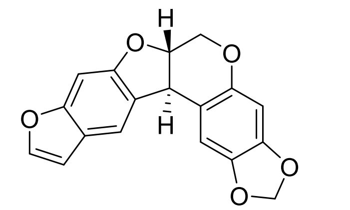


46 (aS)



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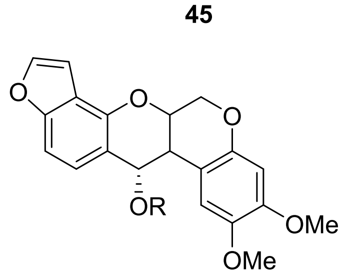
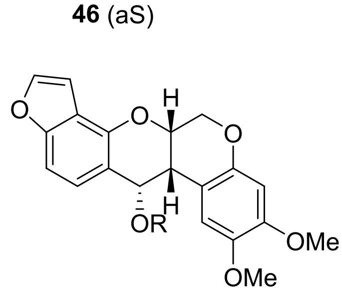
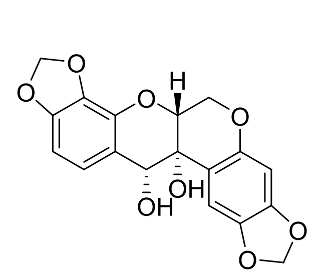


215: R = H
216: R = CH_3



217: R = H
218: R = $COCH_3$



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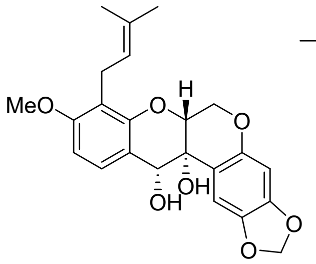

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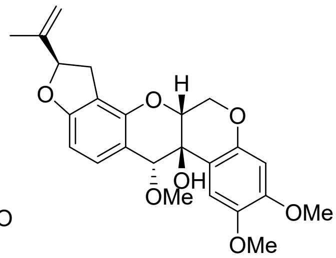

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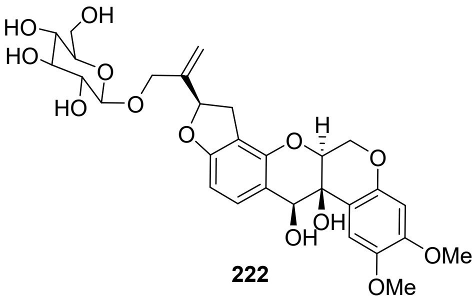

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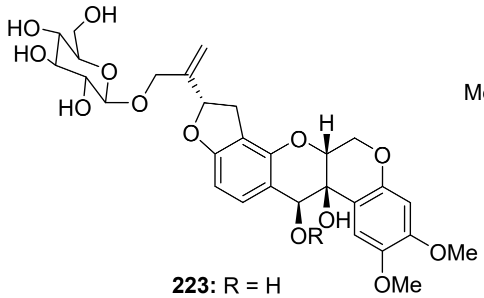
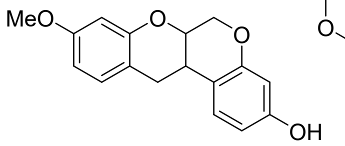


223: R = H
224: R = CH_3



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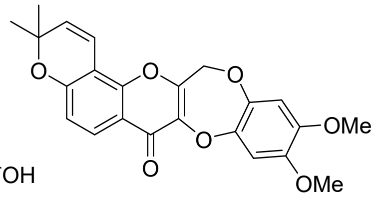

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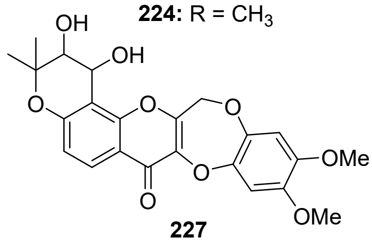

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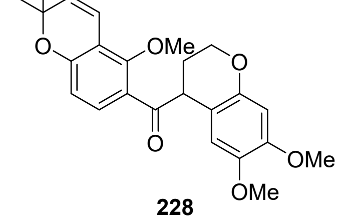

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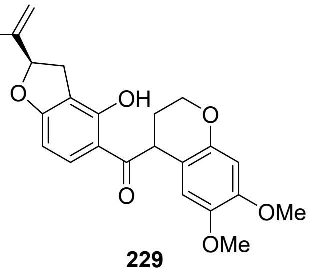

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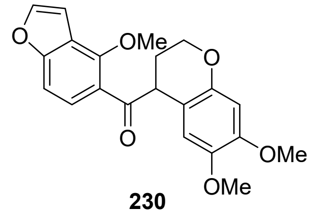

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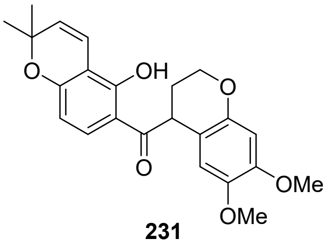

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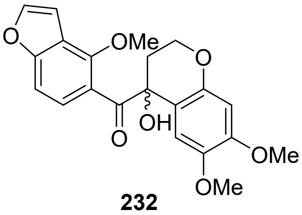

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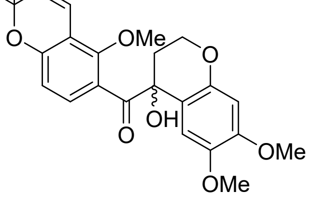

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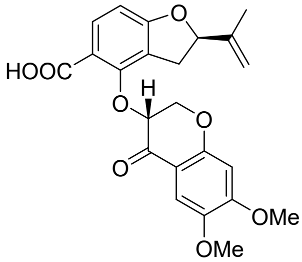

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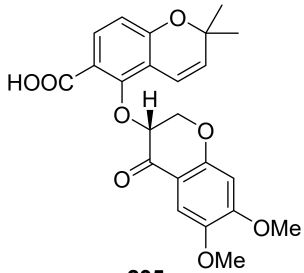

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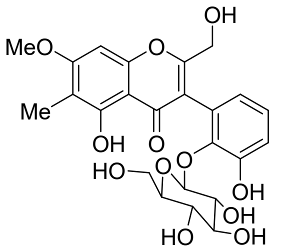
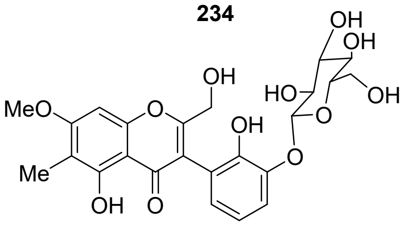


236 (a*S*) and (a*R*)



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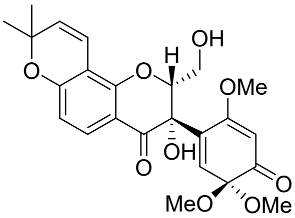

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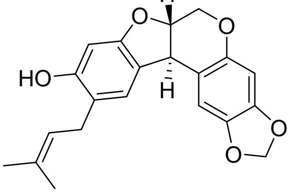

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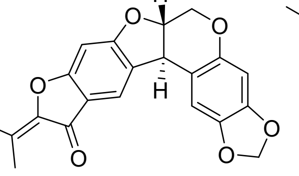

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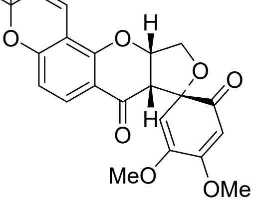

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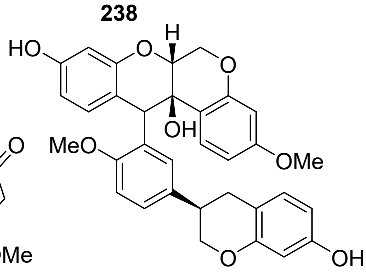

242

Figure S9. Miscellaneous rotenoids: 6a*S*,12a*S*,12*S*-munduserol (**39**),[29] 12-dihydrousararotenoid B (**40**),[85] millettiaosa A (**41**),[86] (–)-13-*homo*-13-oxa-6a,12a-dehydrorotenone (**42**),[20] (+)-13-*homo*-13-*oxa*-6a,12a-dehydrorotenone (**43**),[87] elliptol (**44**),[88] elliptoic acid (**45**),[89] boeravinone Q (**46**),[90] erosurotenoid A (**47**),[14] elliptinol (**215**),[91] 12-deoxo-12α-methoxyelliptone (**216**),[12] 6a*S*,12a*S*,12*S*-elliptinol (**217**),[29] 12-deoxo-12α-acetoxyelliptone (**218**),[28] (12-dihydrousararotenoid A (**219**), 12-dihydrousararotenoid C (**220**)),[85] 12-O-methylrotenolol (**221**),[92] (derieliptosides A (**222**), B (**223**), and C (**224**)),[93] millettiaosa B (**225**),[86] 13-*homo*-13-*oxa*-6a,12a-dehydrodeguelin (**226**),[94] 4′,5′-dihydro-4′,5′-dihydroxy-13-*homo*-13-*oxa*-6a,12a-dehydrodeguelin (**227**),[77] (7a-O-methyldeguelol (**228**), rotenol (**229**)),[95] (7a-*O*-methylelliptonol (**230**), derrisfolins A (**231**), and B (**232**)),[96] 7a-*O*-methyl-12a-hydroxydeguelol (**233**),[97] ((–)-rotoic acid (**234**), (–)-deguoic acid (**235**)),[28] (a*S*)- and (a*R*)-3′,5-dihydroxy-2-hydroxymethyl-7-methoxy-6-methylisoflavone 2′-O-β-D-glucopyranoside (**236**),[90] mirabijalone C (**237**),[53] milletenone A (**238**),[98] erosurotenoids B (**239**), and C (**240**),[14] amorphispironone (**241**),[22] gliricidin (**242**).[71]

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