Phytochemicals of the Genus Maytenus

Subjects: Chemistry, Medicinal

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The genus Maytenus is a member of the Celastraceae family, of which several species have long been used in traditional medicine. Between 1976 and 2021, nearly 270 new compounds have been isolated and elucidated from the genus Maytenus. Among these, maytansine and its homologues are extremely rare in nature. Owing to its unique skeleton and remarkable bioactivities, maytansine has attracted many synthetic endeavors in order to construct its core structure.

Keywords: Maytenus ; triterpenoids ; sesquiterpenes ; alkaloids ; synthesis of maytansine

1. Introduction

Plants of the genus *Maytenus*, a widely distributed member of the Celastraceae family, include approximately 300 plant species that are spread in tropical and subtropical regions of the world [1]. The genus *Maytenus* is widely used in folk medicines around the world, with the roots, bark and leaves being used for the treatment of cancer, gastric ulcers and arthritis because of their anti-inflammatory, analgesic, antiallergic and antitumor properties [2][3][4][5]. Studies have shown that a diverse group of chemical substances, triterpenoids, sesquiterpenes and alkaloids, are responsible for the various biological activities of the plants in this genus [6]. Among them, the macrolide alkaloid, maytansine, was first isolated from *M. serrata* [7], and was shown to be an anti-tumor agent with a novel structure, having some clinical potential. In a clinical trial, maytansine was shown to have promising anti-tumor activities against lymphocytic leukemia, lymphoma, ovarian cancer, breast cancer and melanomas [8][9]. Owing to its unique skeleton and remarkable bioactivity, maytansine has attracted a lot of interest for the possible reconstruction of its core structure. Many synthetic studies of the partial structure of maytansine have been reported. Furthermore, several friedelane triterpenoids with their aromatized characteristic structures and sesquiterpene pyridine alkaloids have been isolated from the genus *Maytenus*, and these have also showed good anti-tumor [10][11] and anti-bacterial [12] characteristics. The new chemical constituents and biological activities of *Maytenus* are given in this review of work from the past 45 years, as well as several chemical synthesis methods of maytansine or maytansine fragments, with the view of realizing their potential development and utilization in the medical field.

2. Chemical Constituents of *Maytenus*

Over the past decades, a large variety of biologically active secondary metabolites have been isolated and identified from the members of the genus *Maytenus*, which include a series of triterpenoids, such as friedelane triterpenoids, lupane triterpenes, oleanane triterpenes, sesquiterpenes and their alkaloids, along with some potent anti-tumor maytansinoids. Many scholars have extensively investigated the species, which belong to the genus *Maytenus*, and they have isolated several novel compounds with a wide variety of structures, which may prove to be useful against different diseases.

2.1. Triterpenoids

The genus *Maytenus* is a rich source of triterpenoids. These types of compounds are characteristic components found in this genus. The known triterpenoids from 1995 to 2005 were summarized by Zhang et al. [13] and Pu et al. [14][15]. Since then, several new triterpenoids have been discovered. Therefore, we have attempted to update all the data relating to the new triterpenoids isolated from the genus *Maytenus* from 1976 to 2021.

2.1.1. Friedelane Friterpenoids

Friedelane triterpenoids are important characteristic components of the Celastraceae family. Moreover, they are endowed with novel chemical diversity and possess a broad spectrum of biological activities. The friedelane triterpenoids are pentacyclic triterpenes composed of 30 carbons, which are converted from oleanolic acid by methyl shifts. In the five six-membered rings, the A/B, B/C and C/D rings are all *trans* and the D/E rings are mostly *cis* (i.e., H-18β). There is one β-CH_3 substitution at each of the C-4, C-5, C-9, C-14 and C-17 positions. The C-3 position is often substituted with a hydroxyl group, although sometimes the hydroxyl group is oxidized to a carbonyl group.

The compound pristimerin (**1**) was isolated from *M. chuchuhuasca* [16]. A new nortriterpene quinone methide, 15*α*-hydroxy-21-keto-pristimerine (**2**), has been obtained from the root bark of *M. catingarum* [17]. Fourteen compounds, including 2,3,22*β*-trihydroxy-24,29-dinor-1,3,5(10), 7-friedelatetraene-6,21-dione-23-al (**3**), 2,22*β*-dihydroxyl-3-methoxy-24,29-dinor-1,3,5(10), 7-friedelatetraene-6,21-dione (**4**), 2,3,22*β*-triihydroxy-23,24,29-trinor-1,3,5(10), 7-friedelatetr aene-6,21-dione (**5**), 2,22*β*-dihydroxyl-3-methoxy-24,29-dinor-1,3,5(10), 7-friedelatetraene-6,21-dione (**6**), 2,3,22*β*-trihydroxy-24,29-dinor-1,3,5(10)-friedelatetraene-6,21-dione (**7**), 2,15*α*,22*β*-trihydroxy-3-methoxy-24,29-dinor-1,3,5(10)-friedelatriene-21-one (**8**), 3,22*β*-dihydroxy-24,29-dinor-l(10)-3,5-friedelatriene-2,7,21-trione (**9**), 3,22*β*-dihydroxy-24,29-dinor-l(10), 3,5-friedelatriene-21-one (**10**), 2,3,22*β*-trihydroxy-24,29-dinor-25(9→8)-1,3,5(10), 7-friedelatetraene-21-one-23-al (**11**), 23-oxo-iso-tingenone (**12**), (8*S*)-7,8-dihydro-7-oxo-tingenoe (**13**), (7*S*,8*S*)-7-hydroxy-7,8-dihydro-tingenone (**14**), (8*S*)-7,8-dihydro-6-oxo-tingenol (**15**) and 23-nor-6-oxo-tingenol (**16**) were isolated from the roots of *M. amazonica* [18] [19]. Compounds 28-hydroxy-friedelane-1,3-dione (**17**) and macrocarpins A–D (**18**–**21**) were obtained from the roots of *M. macrocarpa* [20][21], while maytenfolone (**22**) has been isolated from *M. diversifolia* [22]. Three compounds 6-oxo-iguesterol (**23**), 6-oxo-tingenol (**24**) and 3-*O*-methoxy-6-oxo-tingenol (**25**) have been obtained from the root bark of *M. canariensis* [12]. Four new triterpenes blepharotriol (**26**), 6-deoxoblepharodol (**27**), isoblepharodol (**28**) and 7-oxo-blepharodol (**29**) were separated from *M. blepharodes* [23].

Compounds 15α-hydroxy-tingenone (**30**), 15-dehydro-pristimerin (**31**), vitideasin (**32**) and 20*β*-hydroxy-scutione (**33**) were separated from the roots of *M. vitis-idaea* [24]. Six new compounds, including 7-oxo-7, 8-dihydro-scutione (**34**), 6,23-dioxo-7,8-dihydro-pristimerol-23-oic Acid (**35**), 23-nor-blepharodol (**36**), 3-methoxy-6-oxo-tingenol-23-oic Acid (**37**), retusonine (**38**) and 21-Oxopristimerine (**39**) were isolated from the root bark of *M. retusa* [25]. A new compound 3-*O*-Methyl-6-oxo-pristimerol (**40**) has been isolated from the hexane/Et_2O 1:1 extract of the root bark of *M. chubutensis* [26]. Compounds 3*β*,24-epoxy-2*α*,3*α*-dihydroxy-D:A-friedooleanan-29-oic acid methyl ester (**41**), 2*α*-acetoxy-3*β*,24-epoxy-3*α*-hydroxy-D:A-friedooleanan-29-oic acid methyl ester (**42**), 3*α*-hydroxy-D:A-friedooleanan-28-oic acid (**43**) and 3-oxo-D:A-friedooleanan-28,30-olide (**44**) were obtained from the root bark of *M. jelskii* [27]. Compounds 3*β*,11*β*-dihydroxyfriedelane (**45**) and 3,4-seco-friedelan-3,11*β*-olide (**46**) have been obtained from the hexane extracts of the leaves of *M. robusta* [28], while (16*β*)-16-hydroxy-pristimerin (**47**) was from *M. salicifolia* [29]. A new triterpenoid, 12,16-dihydroxyfriedelan-3-one (**48**), was isolated from an ethyl acetate extract of *M. oblongata* [30]. Compounds 3*β*,24*β*-epoxy-29-methoxy-2*α*,3*α*,6*α*-trihydroxy-D:A-friedelane (**49**) and 3*β*,24*β*-epoxy-29-methoxy-2*α*,3*α*,6*α*-triacetoxy-D:A-friedelane (**49a**) were obtained from the root bark extracts of *M. cuzcoina* [31]. Three new pentacyclic triterpenoids, friedel-1-en-3,16-dione (**50**), 1*α*,29-dihydroxyfriedelan-3-one (**51**) and 16*β*,28,29-trihydroxyfriedelan-3-one (**52**) have been separated from *M. robusta* [32]. Dispemroquinone (**53**) was isolated from *M. dispermus* [33]. A new norquinonemethide triterpene with a netzahualcoyene type skeleton, scutione (**54**), was isolated from the root bark of *M. scutioides* [34]. Compounds zeylasterone (**55**) and demethylzeylasterone (**56**) were obtained from *M. blepharodes* [35], and compound 3,15-dioxo-21*α*-hydroxy friedelane (**57**) was isolated from the methanol extracts of *M. robusta* [36]. Maytenfoliol (**58**) was separated from *M. diversifolium* [37]. Four new cytotoxic triterpenoid dimers, including cangorosin A (**59**), atropcangorosin A (**60**), dihydroatropcangorosin A (**61**) and cangorosin B (**62**) were obtained from the extracts of *M. ilicifolia* [38]. Two new triterpenes, umbellatin *α* (**63**) and umbeilatin *β* (**64**), have been separated from *M. umbellata* [39]. Two novel trimer triscutins, A and B (**65**–**66**), have been isolated from extracts of the root bark of *M. scutioides* [40]. Four new triterpene dimers, xuxuarine E*α* (**67**), scutionin *α*B (**68**), 6′,7′-dihydro-scutionin *α*B (**69**) and 6′*β*-methoxy-6′,7′dihydro-scutionin *α*B (**70**), have been isolated from the extracts of the roots of *M. blepharodes* and *M. magellanica* [41][42] (**Table 1** and **Figure 1**).

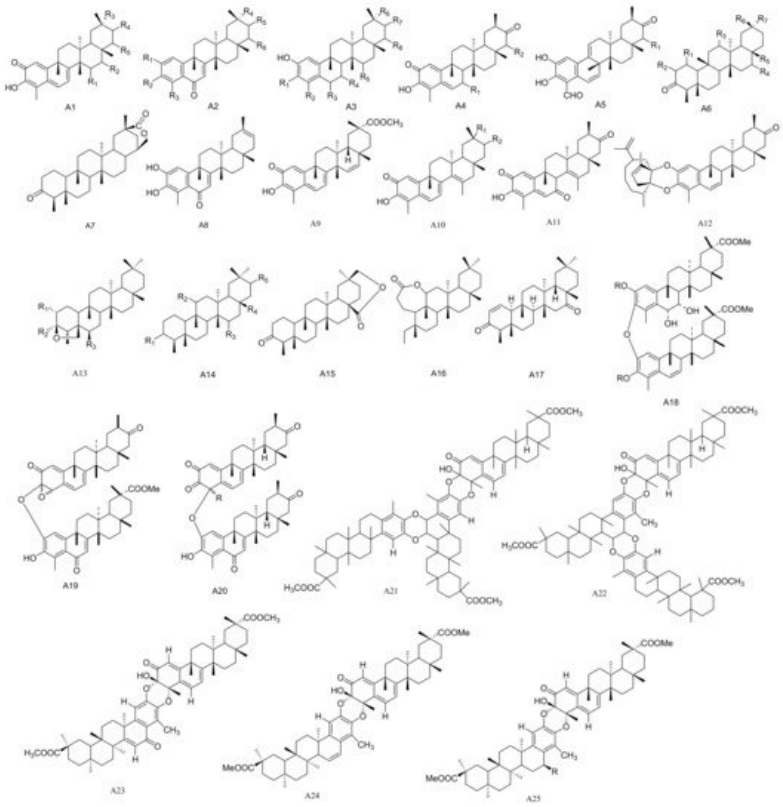


Figure 1. Twenty-five types (A1–A25) of friedelane triterpenoids skeletons.

Table 1. The friedelane triterpenes isolated from *Maytenus*.

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
1	Pristimerin	H	H	COOMe	H	H	-	-	-	A1	[16]
2	15*α*-hydroxy-21-keto-pristimerine	*α*-OH	H	COOMe	=O	H	-	-	-	A1	[17]
3	2,3,22*β*-trihydroxy-24,29-dinor-1,3,5(10),7-friedelatetraene-6,21-dione-23-al	OH	OH	CHO	H	=O	*β*-OH	-	-	A2	[18]
4	2,22*β*-dihydroxyl-3-methoxy-24,29-dinor-1,3,5(10),7-friedelatetraene-6,21-dione	OH	OH	CH_3	H	=O	*β*-OH	-	-	A2	[18]
5	2,3,22*β*-triihydroxy-23,24,29-trinor-1,3,5(10),7-friedelatetraene-6,21-dione	OH	OH	H	H	=O	*β*-OH	-	-	A2	[18]
6	2,22*β*-dihydroxyl-3-methoxy-24,29-dinor-1,3,5(10),7-friedelatetraene-6,21-dione	OH	OCH_3	CH_3	H	=O	*β*-OH	-	-	A2	[18]
7	2,3,22*β*-trihydroxy-24,29-dinor-1,3,5(10)–friedelatetraene -6,21-dione	OH	CH_3	=O	H	H	H	=O	*β*-OH	A3	[18]
8	2,15*α*,22*β*-trihydroxy-3-methoxy-24,29-dinor-1,3, 5(10)-friedelatriene-21-one	OCH_3	CH_3	H	H	*α*-OH	H	=O	*β*-OH	A3	[18]
9	3,22*β*-dihydroxy-24,29-dinor-l(10)-3,5-friedelatriene-2,7,21-trione	=O	*β*-OH	=O	H	-	-	-	-	A4	[18]

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
10	3,22*β*-dihydroxy-24,29-dinor-l(10),3,5–friedelatriene-21-one	H	*β*-OH	=O	H	-	-	-	-	A4	[18]
11	2,3,22*β*-trihydroxy-24,29-dinor-25(9→8)-1,3,5(10),7-friedelatetraene-21-one-23-al	*β*-OH	-	-	-	-	-	-	-	A5	[18]
12	23-oxo-iso-tingenone	H	-	-	-	-	-	-	-	A5	[19]
13	(8*S*)-7,8-dihydro-7-oxo-tingenoe	=O	H	=O	H	-	-	-	-	A4	[19]
14	(7*S*, 8*S*)-7-hydroxy-7,8-dihydro-tingenone	*α*-OH	H	=O	H	-	-	-	-	A4	[19]
15	(8*S*)-7,8-dihydro-6-oxo-tingenol	OH	CH_3	=O	H	H	H	=O	H	A3	[19]
16	23-nor-6-oxo-tingenol	OH	OH	H	H	=O	H	-	-	A2	[19]
17	28-hydroxy-friedelane-1,3-dione	=O	H	H	H	CH_2OH	CH_3	CH_3	-	A6	[20]
18	Macrocarpin A	OH	CHO	=O	H	H	COOMe	H	H	A3	[21]
19	Macrocarpin B	OH	OH	COOH	H	=O	*β*-OH	-	-	A2	[21]
20	Macrocarpin C	OH	OCH3	COOH	H	=O	*β*-OH	-	-	A2	[21]
21	Macrocarpin D	*α*-OH	*β*-OH	=O	H	-	-	-	-	A4	[21]
22	Maytenfolone	-	-	-	-	-	-	-	-	A7	[22]
23	6-oxo-iguesterol	-	-	-	-	-	-	-	-	A8	[12]
24	6-oxo-tingenol	OH	OH	CH_3	H	=O	H	-	-	A2	[12]
25	3-*O*-methoxy-6-oxo-tingenol	OH	OCH_3	CH_3	H	=O	H	-	-	A2	[12]
26	Blepharotriol	OH	OH	OH	COOMe	H	H	-	-	A2	[23]
27	6-deoxoblepharodol	OH	CH_3	H	H	H	COOMe	H	H	A3	[23]
28	Isoblepharodol	OH	CH_3	H	=O	H	COOMe	H	H	A3	[23]
29	7-oxo-blepharodol	OH	CH_3	=O	=O	H	COOMe	H	H	A3	[23]
30	15*α*-hydroxy-tingenone	*α*-OH	H	H	=O	H	-	-	-	A1	[24]
31	15-dihydro-pristimerin	-	-	-	-	-	-	-	-	A9	[24]
32	Vitideasin	*α*-$COOCH_3$	H	-	-	-	-	-	-	A10	[24]
33	20*β*-hydroxy-scutione	*α*-OH	=O	-	-	-	-	-	-	A10	[24]
34	7-oxo-7,8-dihydro-scutione	-	-	-	-	-	-	-	-	A11	[25]
35	6,23-dioxo-7,8-dihydro-pristimerol-23-oic Acid	OH	COOH	=O	H	H	COOMe	H	H	A3	[25]
36	23-nor-blepharodol	OH	H	=O	H	H	COOMe	H	H	A3	[25]
37	3-methoxy-6-oxo-tingenol-23-oic Acid	OH	OCH_3	COOH	H	=O	H	-	-	A2	[25]
38	Retusonine	-	-	-	-	-	-	-	-	A12	[25]
39	21-Oxopristimerine	H	H	COOMe	=O	H	-	-	-	A1	[25]
40	3-*O*-methyl-6-oxo-pristimerol	OH	OCH_3	CH_3	COOMe	H	H	-	-	A2	[26]

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
41	3*β*,24-epoxy-2*α*,3*α*-dihydroxy-D:A-friedooleanan-29-oic acid methyl ester	OH	OH	H	-	-	-	-	-	A13	[27]
42	2*α*-acetoxy-3*β*,24-epoxy-3*α*-hydroxy- D:A-friedooleanan-29-oic acid methyl ester	OAc	OH	H	-	-	-	-	-	A13	[27]
43	3*α*-hydroxy- D:A-friedooleanan-28-oic acid	*α*-OH	H	H	COOH	H	-	-	-	A14	[27]
44	3-oxo-D:A-friedooleanan-28,30-olide	-	-	-	-	-	-	-	-	A15	[27]
45	3*β*,11*β*-dihydroxyfriedelane	*β*-OH	*β*-OH	H	CH_3	H	-	-	-	A14	[28]
46	3,4-seco-friedelan-3,11*β*-olide	-	-	-	-	-	-	-	-	A16	[28]
47	(16*β*)-16-hydroxy-pristimerin	H	*β*-OH	COOMe	H	H	-	-	-	A1	[29]
48	12,16-dihydroxyfriedelan-3-one	H	H	*α*-OH	*β*-OH	CH_3	CH_3	CH_3	-	A6	[30]
49	3*β*,24*β*-epoxy-29-methoxy-2*α*,3*α*,6*α*-trihydroxy-D:A-friedelane	OH	OH	*β*-OH	-	-	-	-	-	A13	[31]
49a	3*β*,24*β*-epoxy-29-methoxy-2*α*,3*α*,6*α*-triacetoxy-D:A-friedelane	OAc	OAc	*β*-OAc	-	-	-	-	-	A13	[31]
50	Friedel-1-en-3,16-dione	-	-	-	-	-	-	-	-	A17	[32]
51	1*α*,29-dihydroxyfriedelan-3-one	*α*-OH	H	H	H	CH_3	CH_3	CH_2OH	-	A6	[32]
52	16*β*,28,29-trihydroxyfriedelan-3-one	H	H	H	*β*-OH	CH_2OH	CH_3	CH_2OH	-	A6	[32]
53	Dispemroquinone	=O	H	H	COOMe	-	-	-	-	A5	[33]
54	Scutione	H	=O	-	-	-	-	-	-	A10	[34]
55	Zeylasterone	OH	OH	COOH	COOMe	H	H	-	-	A2	[35]
56	Demethylzeylasterone	OH	OH	COOH	COOH	H	H	-	-	A2	[35]
57	3,15-dioxo-21-hydroxy friedelane	=O	H	=O	CH_3	*α*-OH	-	-	-	A14	[36]
58	Maytenfoliol	H	H	H	H	CH_2OH	CH_2OH	CH_3	-	A6	[37]
59	Cangorosin A	H	-	-	-	-	-	-	-	A18	[38]
60	Atropcangorosin A	H(atropisomer of 7-bu)	-	-	-	-	-	-	-	A18	[38]
61	Dihydroatropcangorosin A	6′,7′-dihydro derivative of 8-BU	-	-	-	-	-	-	-	A18	[38]
62	Cangorosin B	-	-	-	-	-	-	-	-	A19	[38]
63	Umbellatin *α*	*α*-Me	-	-	-	-	-	-	-	A20	[39]
64	Umbeilatin *β*	*β*-Me	-	-	-	-	-	-	-	A20	[39]

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
65	Triscutin A	-	-	-	-	-	-	-	-	A21	[40]
66	Triscutin B	-	-	-	-	-	-	-	-	A22	[40]
67	Xaxuanine EB	-	-	-	-	-	-	-	-	A23	[41]
68	Scutionin αB	-	-	-	-	-	-	-	-	A24	[42]
69	6′,7′-dihydro-scutionin αB	H	-	-	-	-	-	-	-	A25	[42]
70	6′,7′dihydro-scutionin αB	OCH_3	-	-	-	-	-	-	-	A25	[42]

2.2. Lupane Triterpenes

Lupane triterpenes are characterized by the combination of C-21 and C-19, clustered into a five-membered carbocycle E ring. There is an isopropyl group substituted at the 19th position of the E ring with an *α* configuration, as well as a double bond at the C-20(29) position. The rings of the A/B, B/C, C/D and D/E types are all *trans*. The new triterpenes 3*β*,28,30-Lup-20(29)-ene triol (**71**) and 28,30-Dihyroxylup-20(29)-ene-3-one (**72**) were obtained from *M. canariensis* [43], while compound maytefolin A (**73**) was isolated from the leaves of a Brazilian medicinal plant, *M. ilicifolia* [44]. 3-oxo-lup-20(29)-en-30-al (**74**), 30-hydroxylup-20(29)-en-3-one (**75**), (11*α*)-11-hydroxylup-20(29)-en-3-one (**76**) and (3*β*)-lup-20(30)-ene-3,29-diol (**77**) have been obtained from the hexane extracts of the stems and branches of *M. imbricate* [45]. Compounds 11*α*-hydroxy-*epi*-betuin (**78**), 6*β*-hydroxybetulin (**79**), 24-hydroxybetulin (**80**), rigidenol-28-aldehyde (**81**) and 28-hydroxyglochidone (**82**) have been isolated from *M. cuzcoina* and *M. chiapensis* [46]. Compounds 11*α*-hydroxy-glochidone (**83**), 3-*epi*-nepeticin (**84**) and 3-*epi*-calenduladiol (**85**) were separated from the root barks of *M. cuzcoina* and the leaves of *M. chiapensis* [47]. Four new triterpenes, including 3*α*,16*β*,28-Trihydroxylup-20(29)-ene (**86**), 3*α*,16*β*-dihydroxylup-12-ene (**87**), 3*β*,16*β*-dihydroxylup-12-ene (**88**) and 16*β*-3,4-Secolup-20(29)-en-3-oic acid (**89**), were obtained from the aerial parts of *M. apurimacensis* [48], while compound 3-(*E*)-*β*-coumaroylnepeticin (**90**) was isolated from *M. retusa* [25]. Compound 3,4-*seco*-lupa-4(23): 20(29)-diene-3,28-dioic acid 28-methyl ester (**91**) has been separated from the hexane/Et_2O 1:1 extracts of the root barks of *M. magellanica* [26]. 1*β*-Hydroxy-3*β*-caffeate lup-20(29)-ene (**92**) was isolated from the roots of *M. apurimacensis* [49]. Compounds 3-oxo-21*β*-*H*-hop-22(29)-ene (**93**), 3*β*-hydroxy-21*β*-*H*-hop-22(29)-ene (**94**) and 3,4-seco-21*β*-*H*-hop-22(29)-en-3-oic acid (**95**) were isolated from the leaves of *M. robusta* [28] (**Table 2** and **Figure 2**).

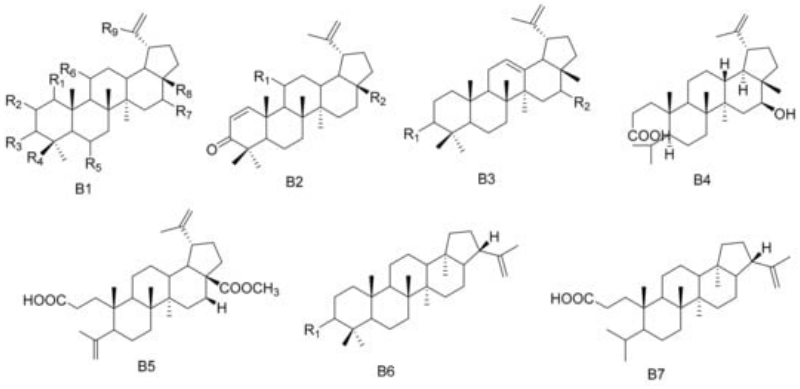


Figure 2. Seven types (B1–B7) of lupane triterpenes skeletons.

Table 2. The lupane triterpenes isolated from *Maytenus*.

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	Type	Ref
71	3*β*,28,30-Lup-20(29)-ene triol	H	H	OH	CH_3	H	H	H	CH_2OH	CH_2OH	B1	[43]
72	28,30-Dihyroxylup-20(29)-ene-3-one	H	H	=O	CH_3	H	H	H	CH_2OH	CH_2OH	B1	[43]
73	Maytefolins A	H	*α*-OH	=O	CH_3	H	H	H	CH_2OH	CH_3	B1	[44]
74	3-oxolup-20(29)-en-30-al	H	H	=O	CH_3	H	H	H	CH_3	CHO	B1	[45]
75	30-hydroxylup-20(29)-en-3-one	H	H	=O	CH_3	H	H	H	CH_3	CH_2OH	B1	[45]
76	(11*α*)-11-hydroxylup-20(29)-en-3-one	H	H	=O	CH_3	H	*α*-OH	H	CH_3	CH_3	B1	[45]
77	(3*β*)-lup-20(30)-ene-3,29-diol	H	H	*β*-OH	CH_3	H	H	H	CH_3	CH_2OH	B1	[45]
78	11*α*-hydroxy-*epi*-betuin	H	H	*α*-OH	CH_3	H	*α*-OH	H	CH_2OH	CH_3	B1	[46]
79	6*β*-hydroxybetulin	H	H	*β*-OH	CH_3	*β*-OH	H	H	CH_2OH	CH_3	B1	[46]
80	24-hydroxybetulin	H	H	=O	CH_2OH	H	H	H	CH_2OH	CH_3	B1	[46]

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9	Type	Ref
81	Rigidenol-28-aldehyde	H	H	=O	CH_3	H	α-OH	H	CHO	CH_3	B1	[46]
82	28-hydroxyglochidone	H	CH_2OH	-	-	-	-	-	-	-	B2	[46]
83	11α-hydroxy-glochidone	α-OH	CH_3	-	-	-	-	-	-	-	B2	[47]
84	3-*epi*-nepeticin	H	H	α-OH	CH_3	H	α-OH	H	CH_3	CH_3	B1	[47]
85	3-*epi*-calenduladiol	H	H	α-OH	CH_3	H	H	H	OH	CH_3	B1	[47]
86	3α,16β,28-Trihydroxylup-20(29)-ene	H	H	α-OH	CH_3	H	H	β-OH	CH_2OH	CH_3	B1	[48]
87	3α,16β-dihydroxylup-12-ene	α-OH	β-OH	-	-	-	-	-	-	-	B3	[48]
88	3β,16β-dihydroxylup-12-ene	β-OH	β-OH	-	-	-	-	-	-	-	B3	[48]
89	16β-3,4-*seco*lup-20(29)-en-3-oic acid	-	-	-	-	-	-	-	-	-	B4	[48]
90	3-(*E*)-β-coumaroylnepeticin	H	H		CH_3	H	α-OH	H	CH_3	CH_3	B1	[25]
91	3,4-*seco*-lupa-4(23):20(29)-diene-3,28-dioicacid 28-methyl ester	-	-	-	-	-	-	-	-	-	B5	[26]
92	1β-Hydroxy-3β-caffeate lup-20(29)-ene	β-OH	H	OCaf	CH_3	H	H	H	CH_3	CH_3	B1	[49]
93	3-oxo-21β-*H*-hop-22(29)-ene	=O	-	-	-	-	-	-	-	-	B6	[28]
94	3β-hydroxy-21β-*H*-hop-22(29)-ene	β-OH	-	-	-	-	-	-	-	-	B6	[28]
95	3,4-*seco*-21β-*H*-hop-22(29)-en-3-oic acid	-	-	-	-	-	-	-	-	-	B7	[28]

2.1.3. Oleanane Triterpenes

Oleanane triterpenes are widely distributed in the plant kingdom. The configuration of the rings is A/B, B/C and C/D, and they are all of the *trans* configuration, while the D/E ring is *cis*. There are eight methyl groups on the core nuclei, and the methyl groups at positions C-10, C-8 and C-17 are all *β* configuration. The methyl group at the C-14 position is *α* configuration, while the C-4 and C-20 positions each have two methyl groups. There may also be other substituents present in the molecule. Two new oleanane triterpenes, 3*β*,19*α*-dihydroxyolean-12-en-29-oic acid (**96**) and 3*α*,19*α*-dihydroxyolean-12-en-29-oic acid (**97**), were obtained from *M. austyoyunnanensis* [14]. Compound 3-oxo-11*α*-methoxyolean-12-ene (**98**) was obtained from the extracts of the roots of *M. spinosa* [24], while 22*α*-hydroxy-29-methoxy-3*β*-tetradecanoate-olean-12-ene (**99**) was separated from the root bark extracts of *M. cuzcoina* [31]. The new compound maytefolin B (**100**) was separated from the leaves of a Brazilian medicinal plant, *M. ilicifolia* [44]. One new triterpene, 3*β*-peroxy-7*β*,25-epoxy-D:B-friedoolean-5-ene (**101**), was separated from the aerial parts of *M. apurimacensis* [48]. Compounds krukovines A (28-hydroxyolean-12-ene-3,11-dione) (**102**) and krukovines C (6*β*,28-dihydroxyolean-12-ene-3,11-dione) (**103**) have been obtained from a South American medicinal plant known as “chuchuhuasi” (*M. krukovii*) [50]. The aerial parts of *M. undata* yielded four new 12-oleanene and 3,4-*seco*-12-oleanene triterpene acids, namely, 3-oxo-11*α*-methoxyolean-12-ene-30-oic acid (**104**), 3-oxo-11*α*-hydroxyolean-12-ene-30-oic acid (**105**), 3-oxo-olean-9(11), 12-diene-30-oic acid (**106**) and 3,4-*seco*-olean-4(23), 12-diene-3,29-dioic acid (**107**) [51], while 3*α*-22*β*-dihydroxyolean-12-en-29-oicacid (**108**) was obtained from the methanol extracts of the barks of *M. laevis* [52]. Compound olean-9(11):12-dien-3*β*-ol (**109**) was isolated from the roots of *M. acanthophylla* [53] and compound 3*β*-hydroxy-D:B-friedo-olean-5-ene (**110**) was isolated from *M. salicifolia* Reissek [54]. Compound 19*α*-hydroxy-3-olean-12-en-29-oic acid (**111**) was isolated from *M. austyoyunnanensis* [55] (**Table 3** and **Figure 3**).

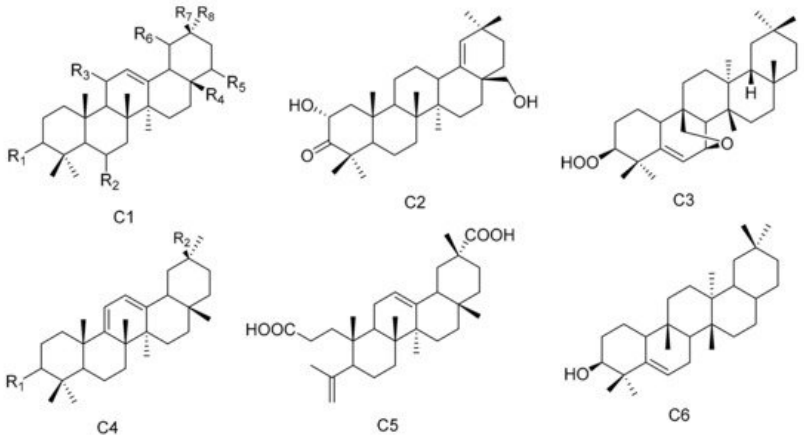


Figure 3. Six types (C1–C6) of oleanane triterpenes skeletons.

Table 3. The oleanane triterpenes isolated from *Maytenus*.

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
96	3*β*,19*α*-dihydroxyolean-12-en-29-oic acid	*β*-OH	H	H	CH_3	H	*α*-OH	CH_3	COOH	C1	[14]
97	3*α*,19*α*-dihydroxyolean-12-en-29-oic acid	*α*-OH	H	H	CH_3	H	*α*-OH	CH_3	COOH	C1	[14]
98	3-oxo-11*α*-methoxyolean-12-ene	=O	H	*α*-OCH_3	CH_3	H	H	CH_3	CH_3	C1	[24]
99	22*α*-hydroxy-29-methoxy-3*β*-tetradecanoate-olean-12-ene	*β*-$COOC_{13}H_{27}$	H	H	CH_3	*α*-OH	H	CH_3	COOMe	C1	[31]
100	Maytefolin B	-	-	-	-	-	-	-	-	C2	[44]
101	3*β*-peroxy-7*β*,25-epoxy-D:B-friedoolean-5-ene	-	-	-	-	-	-	-	-	C3	[48]
102	28-hydroxyolean-12-ene-3,11-dione	=O	H	=O	CH_2OH	H	H	CH_3	CH_3	C1	[50]
103	6*β*,28-dihydroxyolean-12-ene-3,11-dione	=O	*β*-OH	=O	CH_2OH	H	H	CH_3	CH_3	C1	[50]
104	3-oxo-11*α*-methoxyolean-12-ene-30-oic acid	=O	H	α-OCH_3	CH_3	H	H	COOH	CH_3	C1	[51]
105	3-oxo-11*α*-hydroxyolean-12-ene-30-oic acid	=O	H	α-OH	CH_3	H	H	COOH	CH_3	C1	[51]
106	3-oxo-olean-9(11),12-diene-30-oic acid	=O	COOH	-	-	-	-	-	-	C4	[51]
107	3,4-*seco*-olean-4(23),12-diene-3,29-dioic acid	-	-	-	-	-	-	-	-	C5	[51]
108	3*α*-22*β*-dihydroxyolean-12-en-29-oicacid	*α*-OH	H	H	CH_3	*β*-OH	H	CH_3	COOH	C1	[52]
109	Olean-9 (11):12-dien-3*β*-ol	*β*-OH	CH_3	-	-	-	-	-	-	C4	[53]
110	3*β*-Hydroxy-D:B-friedo-olean-5-ene	-	-	-	-	-	-	-	-	C6	[54]
111	19*α*-hydroxy-3-olean-12-en-29-oic acid	=O	H	H	CH_3	H	*α*-OH	CH_3	COOH	C1	[55]

2.1.4. Other Triterpenes

In addition to the above, other types of triterpene compounds have also been isolated from *Maytenus*. These include triterpene dimers, ursane triterpenes and dammarane triterpenes. The compound 3-Oxo-methoxyurs-12-ene (**112**) was isolated from *M. spinosa* [24]. Three ursane triterpenes, krukovines B, D and E (**113**–**115**), were obtained from *M. krukovii* [50]. Compound maytefolin C (**116**) has been isolated from the leaves of *M. ilicifolia* [44], while 28-hydroxy-12-ursene-3*β*-yl-

caffeate (uvaol-3-caffeate) (**117**) has been isolated from the methanol extracts of the barks of *M. laevis* [52]. An ursane triterpene 3*β*-stearyloxy-urs-12-ene (**118**) was obtained from *M. salicifolia* [56]. The stem bark exudates of *M. macrocarpa* yielded ten dammarane triterpenes, namely, 24-(*E*)-3-oxo-dammara-20,24-dien-26-al (**119**), 24-(*Z*)-3-oxo-dammara-20,24-dien-26-al (**120**), 24-(*E*)-3-oxo-dammara-20,24-dien-26-ol (**121**), 24-(*E*)-3-oxo-dammara-23-*α*-hydroxy-20,24-dien-26-al (**122**), 24-(*E*)-3-oxo-dammara-23-*β*-hydroxy-20,24-dien-26-al (**123**), 24-(*E*)-3-oxo-dammara-6-*β*-hydroxy-20, 24-dien-26-al (**124**), 24-(*E*)-3-oxo-dammara-6-*β*-hydroxy-20,24-dien-26-ol (**125**), 23-(*Z*)-3, 25-dioxo-25-nor-dammara-20,24-diene (**126**), 24-(*E*)-3-oxo-23-methylene-dammara-20,24-dien-26-oico (**127**), 24(*Z*)-3-oxodammara20(21),24-dien-27-oic acid (**128**) and octa-nor-13-hydroxydammara-1-en-3,17-dione (**129**). This was in 1997, and it was the first time that dammrane triterpenes were isolated from Celastraceae [57][58] (**Table 4** and **Figure 4**).

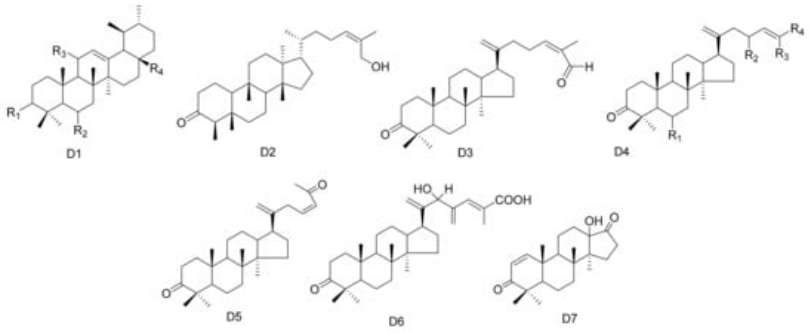
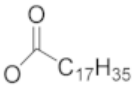


Figure 4. Seven types (D1–D7) of other triterpenes skeletons.

Table 4. The other triterpenes isolated from *Maytenus*.

No.	Name	R_1	R_2	R_3	R_4	Type	Ref.
112	**3-Oxo-methoxyurs-12-ene**	**=O**	**H**	***α*-OCH_3**	**CH_3**	**D1**	**[24]**
113	**Krukovines B**	**=O**	**H**	**CH_2OH**	**H**	**D1**	**[50]**
114	**Krukovines D**	**=O**	**OH**	**CH_2OH**	**H**	**D1**	**[50]**
115	**Krukovines E**	**=O**	**H**	**OH**	**H**	**D1**	**[50]**
116	**Maytefolins C**	**-**	**-**	**-**	**-**	**D2**	**[44]**
117	**28-hydroxy-12-ursene-3*β*-yl-caffeate**	***β*-OCaf**	**H**	**CH_2OH**	**H**	**D1**	**[52]**
118	**3*β*-stearyloxy-urs-12-ene**		**H**	**CH_3**	**H**	**D1**	**[56]**
119	**24-(*E*)-3-oxo-dammara-20,24-dien-26-al**	**-**	**-**	**-**	**-**	**D3**	**[57]**
120	**24-(*Z*)-3-oxo-dammara-20,24-dien-26-al**	**-**	**-**	**-**	**-**	**D3**	**[57]**
121	**24-(*E*)-3-oxo-dammara-20,24-dien-26-ol**	**H**	**H**	**CH_3**	**CH_2OH**	**D4**	**[57]**
122	**24-(*E*)-3-oxo-dammara-23-*α*-hydroxy-20,24-dien-26-al**	**H**	***α*-OH**	**CH_3**	**CHO**	**D4**	**[57]**
123	**24-(*E*)-3-oxo-dammara-23-*β*-hydroxy-20,24-dien-26-al**	**H**	***β*-OH**	**CH_3**	**CHO**	**D4**	**[57]**
124	**24-(*E*)-3-oxo-dammara-6-*β*-hydroxy-20,24-dien-26-al**	***β*-OH**	**H**	**CH_3**	**CHO**	**D4**	**[57]**
125	**24-(*E*)-3-oxo-dammara-6-*β*-hydroxy-20,24-dien-26-ol**	***β*-OH**	**H**	**CH_3**	**CH_2OH**	**D4**	**[57]**
126	**23-(*Z*)-3,25-dioxo-25-nor-dammara-20,24-diene**	**-**	**-**	**-**	**-**	**D5**	**[57]**
127	**24-(*E*)-3-oxo-23-methylene-dammara-20,24-dien-26-oico**	**-**	**-**	**-**	**-**	**D6**	**[58]**
128	**24(*Z*)-3-oxodammara20(21),24-dien-27-oic acid**	**H**	**H**	**COOH**	**CH_3**	**D4**	**[58]**
129	**Octa-nor-13-hydroxydammara-1-en-3,17-dione**	**-**	**-**	**-**	**-**	**D7**	**[58]**

2.2. Sesqiterpenoids

The most widespread and characteristic metabolites isolated from the Celastraceae family are a large group of unusual and highly oxygenated sesquiterpenoids, based on the [5,11-epoxy-5*β*,10*α*-eduesman-4(14)-ene] skeleton known as dihydro-*β*-agarofum. Sesquiterpenes have multiple substitution sites in their structure, and common substituents include -

OH, -OAc, -Ofu, -Obz and -Onic, which is due to the diversification of their positions and types. There is a high probability that there are several new compounds from this group that still need to be discovered [59].

Two sesquiterpene polyesters with new polyhydroxy skeletons, 1*α*,9*α*-dibenzoyloxy-6*β*,8*α*,15-triacetoxy-4*β*-hydroxy-dihydro-*β*-agarofurane (**130**) and 1*α*,9*α*-dibenzoyloxy-2*α*,6*β*,8*α*,15-tetracetoxy-4*β*-hydroxydihydro-*β*-agrofurane (**131**), were isolated from the aerial portions of *M. canariensis* [60]. Compounds 6*β*,8*β*-15-triacetoxy-1*α*,9*α*-dibenzoyloxy-4*β*-hydroxy-*β*-dihydroagarofuran (**132**), 1*α*,6*β*,8*β*,15-tetraacetoxy-9*α*-benzoyloxy-4*β*-hydroxy-*β*-dihydroagarofuran (**133**) and (1*S*,4*S*,6*R*,7*R*,8*R*,9*R*)-1,6,15-triacetoxy-8,9-dibenzoyloxy-4*β*-hydroxy-*β*-dihydroagarofuran (**134**) were isolated from the aerial parts of *M. macrocarpa* [61]. Compounds (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6,15-diacetoxy-1,2,9-tribenzoyloxy-4-hrdroxy-8-oxo-dihydro-*β*-agarofuran (**135**) and 9*β*-cinnamoyloxy-2*β*,3*β*-diacetoxy-6*β*-hydroxy-l*α*-nicotinoyloxydihidro-*β*-agarofuran (**136**) were separated from *M. blepharodes* [41]. Eight sesquiterpenoids, including 1*α*-acetoxy-2*α*,6*β*,9*β*-trtifuroyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran (**137**), 1*α*,2*α*-diacetoxy-6*β*,9*β*-difuroyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran (**138**), 1*α*-acetoxy-6*β*,9*β*-difuroyloxy-2*α*,4*β*-dihydroxy-dihydro-*β*-agarofuran (**139**), 1*α*-acetoxy-2*α*-benzoyloxy-6*β*,9*β*-difuroyloxy-4*β*-dihydro-*β*-agarofuran (**140**), 1*α*-acetoxy-6*β*,9*β*-difuroyloxy-2*α*-propyonyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran (**141**), 1*α*-acetoxy-6*α*,9*β*-difuroyloxy-2*α*-(2)-methylbutyroyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran (**142**), 1*α*,2*α*,15-triacetoxy-6*β*,9*β*-difuroyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran (**143**) and 1*α*,2*α*,15-triacetoxy-6*β*,9*β*-dibenzoyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran (**144**) were obtained from the n-hexane: Et_2O (1:1) extracts of the fruits of *M. cuzcoina* [59].

The *n*-hexane/Et_2O (1:1) extracts of the root barks of *M. magellanica* yielded eight new dihydro-*β*-agarofuran sesquiterpenes (**145**–**152**), and the *n*-hexane/Et_2O (1:1) extracts of the root barks of *M. chubutensis* yielded two more new compounds of this family (**153**–**154**). Their structures were elucidated as (1*R*,2*R*,4*S*,5*R*,7*S*,9*S*,10*R*)-2-acetoxy-1-benzoyloxy-9-cinnamoyloxy-4-hydroxy-dihydro-*β*-agarofuran (**145**), (1*R*,2*S*,3*S*,5*R*,7*R*,9*S*,10*R*)-2-acetoxy-9-benzoyloxy-1-cinnamoyloxy-3-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran (**146**), (1*R*,2*S*,3*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-2,6-diacetoxy-1-benzoyloxy-9-cinnamoyloxy-3-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran (**147**), (1*R*,2*S*,3*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-2,6-diacetoxy-1,9-dibenzoyloxy-3-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran (**148**), (1*R*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*,10*R*)-2,3-diacetoxy-8,9-dibenzoyloxy-1-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran (**149**), (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,8*S*,9*R*,10*S*)-6,8-diacetoxy-1,2,9-tribenzoyloxy-4-hydroxy-dihydro-*β*-agarofuran (**150**), (1*R*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*,10*R*)-2,8-diacetoxy-3,9-dibenzoyloxy-1-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran (**151**), (1*R*, 2*S*,4*R*,5*S*,6*R*,7*R*,8*S*,9*R*,10*S*)-6,8-diacetoxy-1,9-dibenzoyloxy-2-nicotinoyloxy-dihydro-*β*-agarofuran (**152**), 1*α*,15-diacetoxy-6*β*,9*β*-dibenzoyloxy-2*α*-nicotinoyloxy-dihydro-*β*-agarofuran (**153**) and 1*α*,15-diacetoxy-6*β*,9*β*-dibenzoyloxy-2*α*-nicotinoyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran (**154**) [62]. Compounds (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-1,2,6,9,15-pentaacetoxy-4-hydroxy-8-oxo-dihydro-*β*-agarofuran (**155**), (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-1,2,9,15-taacetoxy-4,6-dihydroxy-8-oxo-dihydro-*β*-agarofuran (**156**), (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-1,9,15-triacetoxy-2,4,6-trihydroxy-8-oxo-dihydro-*β*-agarofuran (**157**), (1*R*,2*S*,3*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-1,2,3,6,9,12,15-heptaacetoxy-4-hydroxy-8-oxo-dihydro-*β*-agarofuran (**158**) and 1*α*,2*α*,3*β*,6*β*,8*α*,9*α*,12,15-octaacetoxy-4*β*-hydroxy-dihydro-*β*-agarofuran (**159**) were isolated from the leaves of *M. chiapensis* [63]. In addition, (1*S*,4*S*,5*S*,6*R*,7*R*,8*S*,9*R*,10*R*)-8-acetoxy-1,9-dibenzoyloxy-6-nicotynoyloxy-dihydro-*β*-agarofuran (**160**) and (1*S*,4*R*,5*R*,6*R*,7*R*,8*S*,9*R*,10*R*)-8-acetoxy-1,9-dibenzoyloxy-4-hydroxy-nicotynoyloxy-dihydro-*β*-agarofuran (**161**) have been isolated from the roots of *M. apurimacensis* [49].

Thirteen sesquiterpenes, including (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-115-diacetoxy-2,6-dibenzoyloxy-9-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**162**), (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,2,15-triacetoxy-6-benzoyloxy-9-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**163**), (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,15-diacetoxy-6-benzoyloxy-9-(3-furoyloxy)-2,4-dihydroxy-dihydro-*β*-agarofuran (**164**), (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,15-diacetoxy-6,9-dibenzoyloxy-2,4-hydroxy-dihydro-*β*-agarofuran (**165**), (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,2,6,15-tetracetoxy-9-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**166**), (1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1-Acetoxy-2,6-dibenzoyloxy-9-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**167**), (1*S*,2*S*,3*S*,4*S*,5*R*,7*R*,9*S*,10*R*)-2,3-diacetoxy-9-benzoyloxy-1-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**168**), (1*S*,2*R*,4*S*,5*R*,7*R*,9*S*,10*R*)-2-acetoxy-9-benzoyloxy-1-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**169**), (1*S*,2*R*,4*S*,5*R*,7*R*,9*S*,10*R*)-2-Acetoxy-1,9-di-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**170**), (1*S*,2*R*,4*S*,5*R*,7*R*,9*S*,10*R*)-2-Acetoxy-9-trans-cynamoiloxy-1-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**171**), (1*S*,4*S*,5*R*,7*R*,9*S*,10*S*)-9-Benzoyloxy-1-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran (**172**), (1*S*,2*R*,3*R*,4*R*,5*S*,7*R*,9*S*,10*R*)-2,3-diacetoxy-9-benzoyloxy-1-(3-furoyloxy)-dihydro-*β*-agarofuran (**173**) and (1*S*,2*R*,4*R*,5*S*,7*R*,9*S*,10*R*)-2-Acetoxy-9-benzoyloxy-1-(3-furoyloxy)-dihydro-*β*-agarofuran (**174**) have been isolated from the hexanee-Et_2O extracts of the fruits of *M. jelskii* [64]. Nine new *β*-dihydroagarofurans, 1*α*2*α*,9*β*,15-tetracetoxy-8*β*-benzoyloxy-*β*-dihydroagarofuran (**175**), 1*α*-benzoyloxy-2*α*,6*β*,8*α*-triacetoxy-9*α*-methyllbutyroyloxy-*β*-dihydroagarofuran (**176**), 1*α*,6*β*-diacetoxy-2*α*,8*α*,9*α*-tribenzoyloxy-*β*-dihydroagarofuran (**177**), 1*α*-benzoyloxy-2*α*,6*β*,8*α*,9*α*-tetraacetoxy-*β*-dihydroagarofuran (**178**), 1*α*,6*β*,8*α*-triacetoxy-9*α*-benzoyloxy-2*α*-hydroxy-*β*-dihydroagarofuran (**179**), (1*R*,2*S*,4*R*,5*S*,6*R*,7*R*,8*R*,9*S*,10*S*)-1,6-diacetoxy-8,9-dibenzoyloxy-2-h ydroxy-*β*-dihydroagarofuran (**180**), 1*α*,6*β*,15-

triacetoxy-8*α*-methylbutyroyloxy-9*α*-benzoyloxy-2*α*-hydroxy-*β*-dihydroagaro-furan (**181**), 1*α*,6*β*,15-triacetoxy-8*α*,9*α*-dibenzoyloxy-2*α*-hydroxy-*β*-dihydroagarofuran (**182**) and 1*α*,6*β*,8*β*,15-tetracetoxy-2*α*-hydroxy-9*α*-benzoyloxy-*β*-dihydroagarofuran (**183**), were isolated from the leaves of *M. spinosa* [65]. Five new compounds, chiapens A–E (**184**–**188**), were isolated from *M. chiapensis* [66].

Compounds 1*α*,6*β*-diacetoxy-8*α*-hydroxy-9*β*-furoyloxy-*β*-agarofuran (**189**), 1*α*-acetoxy-6*β*,8*α*-dihydroxy-9*β*-furoyloxy-*β*-agarofuran (**190**), 1*α*-benzoyloxy-2*α*,3*β*,6*β*,9*β*,14-pentaacetoxy-8-oxo-*β*-agarofuan (**191**) and 1*α*-furoyloxy-2*α*,3*β*,6*β*,9*β*,14-pentaacetoxy-8-oxo-*β*-agarofuan (**192**) were obtained from an extract of the seeds of *M. boaria* [67]. Bilocularins A−I (**193**–**201**) were isolated from *M. bilocularis*. In addition, bilocularins D–F are the first examples of dihydro-b-agarofurans, which bear a hydroxyacetate group [68][69]. Compounds (1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9,10-trihydroxy-2,2,5*a*,9-tetramethyloctahydro-2*H*-3,9*a*-methanobenzo[*b*]oxepin-5-yl furan-3-carboxylate (**202**), (1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9-dihydroxy-2,2,5*a*,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepine-5,10-diyl bis(furan-3-carboxylate) (**203**), (1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6-acetoxy-9-hydroxy-2,2,5*a*,9-tetramethyloctahydro-2*H*-3,9*a*-methanobenzo[*b*]oxepine-5, 10-diyl bis(furan-3-carboxylate) (**204**) and (1*S*,4*S*,5*S*,6*R*,7*R*,9*S*, 10*S*)-6-acetoxy-10-(benzoyloxy)-9-hydroxy-2,2,5*a*,9-tetramethyloctahydro-2*H*-3,9*a*-methanobenzo[*b*]-oxepin-5-yl furan-3-carboxylate (**205**) were isolated from the seeds of *M. boaria* [70][71]. Compounds 2*β*,6*β*-diacetoxy-1*α*,9*β*-dibenzoyl-3*β*-hydroxy-dihydro-*β*-agarofuran (**206**), 1*α*,2*α*,6*β*,8*α*-tetraacetoxy-9*β*-benzoyl-15-hydroxy-dihydro-*β*-agarofuran (**207**) and 1*α*,2*α*,6*β*,8*α*,15-pentaacetoxy-9*β*-benzoyl-dihydro-*β*-agarofuran (**208**) have been separated from *M. boaria* [72]. 1*β*-acetoxy-9*α*-benzoyloxy-2*β*,6*α*-dinicotinoyloxy-*β*-dihydroagarofuran (**209**) was obtained from the anti-microbially active ethanol extracts of *M. heterophylla* [73]. In addition, an eudesmane glucoside, boarioside (**210**), has been isolated from *M. boaria* [74]. Compounds 4-deacetyl-10-oxo-dihydrobotrydial (**211**) and 4*β*-acetoxy-9*β*,10*β*,15*α*-trihydroxyp robotrydial (**212**) were obtained from solid cultures of an endocytic fungal strain, *Phomopsis* species Lz42, cultivated on *M. hookeri* [75] (**Table 5** and **Figure 5**).

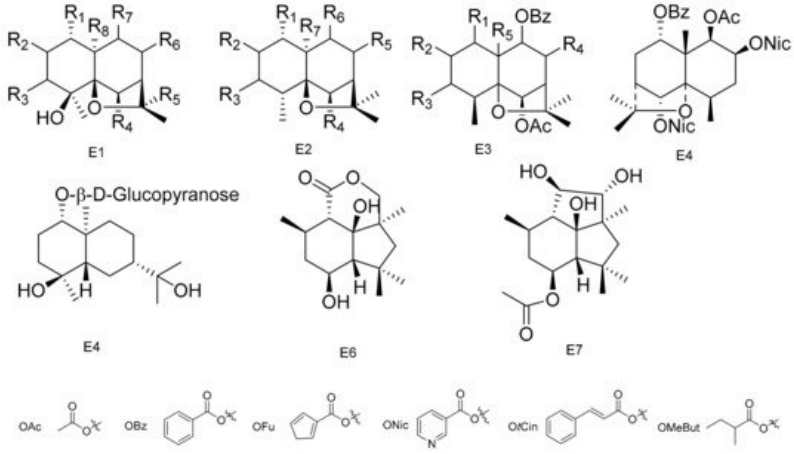


Figure 5. Seven types (E1–E7) of sesqiterpenoids skeletons.

Table 5. The sesqiterpenoids isolated from *Maytenus*.

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
130	**1*α*,9*α*-dibenzoyloxy-6*β*,8*α*,15-triacetoxy-4*β*-hydroxy-dihydro-*β*-agarofurane**	OBz	H	H	OAc	CH_3	*α*-OAc	*α*-OBz	CH_2OAc	E1	[60]
131	**1*α*,9*α*-dibenzoyloxy-2*α*,6*β*,8*α*,15-tetracetoxy-4*β*-hydroxydihydro-*β*-agrofurane**	OBz	*α*-OAc	H	OAc	CH_3	*α*-OAc	*α*-OBz	CH_2OAc	E1	[60]
132	**6*β*,8*β*-15-triacetoxy-1*α*,9*α*-dibenzoyloxy-4*β*-hydroxy-*β*-dihydroagarofuran**	OBz	H	H	OAc	CH_3	*β*-OAc	*α*-OBz	CH_2OAc	E1	[61]
133	**1*α*,6*β*,8*β*-15-tetraacetoxy-9*α*-benzoyloxy-4*β*-hydroxy-*β*-dihydroagarofuran**	OAc	H	H	OAc	CH_3	*β*-OAc	*α*-OBz	CH_2OAc	E1	[61]
134	**(1*S*,4*S*,6*R*,7*S*,8*S*,9*R*)-1,6,15- triacetoxy-8,9-dibenzoyloxy-4*β*-hydroxy-*β*-dihydroagarofuran**	OAc	H	H	OAc	CH_3	*α*-OBz	*β*-OBz	CH_2OAc	E1	[61]
135	**(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6,15-diacetoxy-1,2,9-tribenzoyloxy-4-hrdroxy-8-oxo-dihydro-*β*-agarofuran**	OBz	*α*-OBz	H	OAc	CH_3	O	*α*-OBz	CH_2OAc	E1	[41]

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
136	9*β*-cinnamoyloxy-2*β*,3*β*-diacetoxy-6*β*-hydroxy-l*α*-nicotinoyloxydihidro-*β*-agarofuran	ONic	*β*-OAc	*β*-OAc	OH	CH_3	H	*β*-OCin	CH_3	E1	[41]
137	1*α*-acetoxy-2*α*,6*β*,9*β*-trtifuroyloxy-4*β*-hydroxy-dihydro-*β*- agarofuran	OAc	*α*-OFu	H	OFu	CH_3	H	*β*-OFu	CH_3	E1	[59]
138	1*α*,2*α*-diacetoxy-6*β*,9*β*-difuroyloxy-4*β*-hydroxy-dihydro-*β*- agarofuran	OAc	*α*-OAc	H	OFu	CH_3	H	*β*-OFu	CH_3	E1	[59]
139	1*α*-acetoxy-6*β*,9*β*-difuroyloxy-2*α*,4*β*-dihydroxy-dihydro-*β*-agarofuran	OAc	*α*-OH	H	OFu	CH_3	H	*β*-OFu	CH_3	E1	[59]
140	1*α*-acetoxy-2*α*-benzoyloxy-6*β*,9*β*-difuroyloxy-4*β*-dihydro-*β*-agarofuran	OAc	*α*-OBz	H	OFu	CH_3	H	*β*-OFu	CH_3	E1	[59]
141	1*α*-acetoxy-6*β*,9*β*-difuroyloxy-2*α*-propyonyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OPr	H	OFu	CH_3	H	*β*-OFu	CH_3	E1	[59]
142	1*α*-acetoxy-6*α*,9*β*-difuroyloxy-2*α*-(2)-methylbutyroyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OButMe	H	OFu	CH_3	H	*β*-OFu	CH_3	E1	[59]
143	1*α*, 2*α*,15-triacetoxy-6*β*,9*β*-difuroyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OAc	H	OFu	CH_3	H	*β*-OFu	CH_2OAc	E1	[59]
144	1α, 2α,15-triacetoxy-6β,9β-dibenzoyloxy-4β-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OAc	H	OBz	CH_3	H	*β*-OBz	CH_2OAc	E1	[59]
145	(1*R*,2*R*,4*S*,5*R*,7*S*,9*S*,10*R*)-2-acetoxy-1-benzoyloxy-9-cinnamoyloxy-4-hydroxy-dihydro-*β*-agarofuran	OBz	*β*-OAc	H	H	CH_3	H	*β*-OH	CH_3	E1	[62]
146	(1*R*,2*S*,3*S*,5*R*,7*R*,9*S*,10*R*)-2-acetoxy-9-benzoyloxy-1-cinnamoyloxy-3-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran	OCin	*β*-OAc	*β*-ONic	H	CH_3	H	H	CH_3	E1	[62]
147	(1*R*,2*S*,3*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-2,6-diacetoxy-1-benzoyloxy-9-cinnamoyloxy-3-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran	OBz	*β*-OAc	*β*-ONic	OAc	CH_3	H	*β*-OCin	CH_3	E1	[62]
148	(1*R*,2*S*,3*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-2,6-diacetoxy-1,9-dibenzoyloxy-3-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran	OBz	*β*-OAc	*β*-ONic	H	CH_3	H	*β*-OBz	CH_3	E1	[62]
149	(1*R*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*,10*R*)-2,3-diacetoxy-8,9-dibenzoyloxy-1-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran	ONic	*β*-OAc	*β*-OAc	H	CH_3	*β*-OBz	*β*-OBz	CH_3	E1	[62]
150	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,8*S*,9*R*,10*S*)-6,8-diacetoxy-1,2,9-tribenzoyloxy-4-hydroxy-dihydro-*β*-agarofuran	OBz	*α*-OBz	H	OAc	CH_3	*β*-OAc	*β*-OBz	CH_3	E1	[62]
151	(1*R*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*,10*R*)-2,8-diacetoxy-3,9-dibenzoyloxy-1-nicotinoyloxy-4-hydroxy-dihydro-*β*-agarofuran	ONic	*β*-OAc	*β*-OBz	H	*β*-OAc	*β*-OBz	CH_3	-	E2	[62]
152	(1*R*,2*S*,4*R*,5*S*,6*R*,7*R*,8*S*,9*R*,10*S*)-6,8-diacetoxy-1,9-dibenzoyloxy-2-nicotinoyloxy-dihydro-*β*-agarofuran	OBz	*α*-ONic	H	OAc	*β*-OAc	*β*-OBz	CH_3	-	E2	[62]
153	1*α*,15-diacetoxy-6*β*,9*β*-dibenzoyloxy-2*α*-nicotinoyloxy-dihydro-*β*-agarofuran	OAc	*α*-ONic	H	OBz	H	*β*-OBz	CH_3	-	E2	[62]
154	1*α*,15-diacetoxy-6*β*,9*β*-dibenzoyloxy-2*α*-nicotinoyloxy-4*β*-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-ONic	H	OBz	CH_3	H	*β*-OBz	CH_2OAc	E1	[62]
155	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-1,2,6,9,15-pentaacetoxy-4-hydroxy-8-oxo-dihydro-*β*-agarofuran	OAc	*α*-OAc	H	OAc	CH_3	O	*α*-OAc	CH_2OAc	E1	[63]
156	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-1,2,9,15-taacetoxy-4,6-dihydroxy-8-oxo-dihydro-*β*-agarofuran	OAc	*α*-OAc	H	OH	CH_3	O	*α*-OAc	CH_2OAc	E1	[63]

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
157	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-1,9,15-triacetoxy-2,4,6-trihydroxy-8-oxo-dihydro-*β*-agarofuran	OAc	*α*-OH	H	OH	CH_3	O	*α*-OAc	CH_2OAc	E1	[63]
158	(1*R*,2*S*,3*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-1,2,3,6,9,12,15-heptaacetoxy-4-hydroxy-8-oxo-dihydro-*β*-agarofuran	OAc	*α*-OAc	*β*-OAc	OAc	CH_2OAc	O	*α*-OAc	CH_2OAc	E1	[63]
159	1*α*,2*α*,3*β*,6*β*,8*α*,9*α*,12,15-octaacetoxy-4*β*-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OAc	*β*-OAc	OAc	CH_2OAc	*α*-OAc	*α*-OAc	CH_2OAc	E1	[63]
160	(1*S*,4*S*,5*S*,6*R*,7*R*,8*S*,9*R*,10*R*)-8-acetoxy-1,9-dibenzoyloxy-6-nicotynoyloxy-dihydro-*β*-agarofuran	OBz	H	H	ONic	*α*-OAc	*α*-OBz	CH_3	-	E2	[49]
161	(1*S*,4*R*,5*R*,6*R*,7*R*,8*S*,9*R*,10*R*)-8-acetoxy-1,9-dibenzoyloxy-4-hydroxy-nicotynoyloxy-dihydro-*β*-agarofuran	OBz	H	H	ONic	CH_3	*α*-OAc	*α*-OBz	CH_3	E1	[49]
162	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,15-diacetoxy-2,6-dibenzoyloxy-9-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OBz	H	OBz	CH_3	H	*α*-OFu	CH_2OAc	E1	[64]
163	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,2,15-triacetoxy-6-benzoyloxy-9-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OAc	H	OBz	CH_3	H	*α*-OFu	CH_2OAc	E1	[64]
164	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,15-diacetoxy-6-benzoyloxy-9-(3-furoyloxy)-2,4-dihydroxy-dihydro-*β*-agarofuran	OAc	*α*-OH	H	OBz	CH_3	H	*α*-OFu	CH_2OAc	E1	[64]
165	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,15-diacetoxy-6,9-dibenzoyloxy-2,4-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OH	H	OBz	CH_3	H	*α*-OBz	CH_2OAc	E1	[64]
166	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1,2,6,15-tetracetoxy-9-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OAc	H	OAc	CH_3	H	*α*-OFu	CH_2OAc	E1	[64]
167	(1*R*,2*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*R*)-1-Acetoxy-2,6-dibenzoyloxy-9-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OAc	*α*-OBz	H	OBz	CH_3	H	*α*-OFu	CH_3	E1	[64]
168	(1*S*,2*S*,3*S*,4*S*,5*R*,7*R*,9*S*,10*R*)-2,3-diacetoxy-9-benzoyloxy-1-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OFu	*β*-OAc	*β*-OAc	H	CH_3	H	*α*-OBz	CH_3	E1	[64]
169	(1*S*,2*R*,4*S*,5*R*,7*R*,9*S*,10*R*)-2-acetoxy-9-benzoyloxy-1-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OFu	*β*-OAc	H	H	CH_3	H	*α*-OBz	CH_3	E1	[64]
170	(1*S*,2*R*,4*S*,5*R*,7*R*,9*S*,10*R*)-2-Acetoxy-1,9-di-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OFu	*β*-OAc	H	H	CH_3	H	*α*-OFu	CH_3	E1	[64]
171	(1*S*,2*R*,4*S*,5*R*,7*R*,9*S*,10*R*)-2-Acetoxy-9-trans-cynamoiloxy-1-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OFu	*β*-OAc	H	H	CH_3	H	*α*-OCin	CH_3	E1	[64]
172	(1*S*,4*S*,5*R*,7*R*,9*S*,10*S*)-9-Benzoyloxy-1-(3-furoyloxy)-4-hydroxy-dihydro-*β*-agarofuran	OFu	H	H	H	CH_3	H	*α*-OBz	CH_3	E1	[64]
173	(1*S*,2*R*,3*R*,4*R*,5*S*,7*R*,9*S*,10*R*)-2,3-diacetoxy-9-benzoyloxy-1-(3-furoyloxy)-dihydro-*β*-agarofuran	OFu	*β*-OAc	*β*-OAc	H	H	*α*-OBz	CH_3	-	E2	[64]
174	(1*S*,2*R*,4*R*,5*S*,7*R*,9*S*,10*R*)-2-Acetoxy-9-benzoyloxy-1-(3-furoyloxy)-dihydro-*β*-agarofuran	OFu	*β*-OAc	H	H	H	*α*-OBz	CH_3	-	E2	[64]
175	1*α*,2*α*,9*β*,15-tetracetoxy-8*β*-benzoyloxy-*β*-dihydroagarofuran	OAc	*α*-OAc	H	H	*β*-OBz	*α*-OAc	CH_2OAc	-	E2	[65]
176	1*α*-benzoyloxy-2*α*,6*β*,8*α*-triacetoxy-9α-methyllbutyroyloxy-*β*-dihydroagarofuran	OBz	*α*-OAc	H	OAc	*α*-OAc	*α*-OMeBut	CH_3	-	E2	[65]
177	1*α*,6*β*-diacetoxy-2*α*,8*α*,9*α*-tribenzoyloxy-*β*-dihydroagarofuran	OAc	*α*-OBz	H	OAc	*α*-OBz	*α*-OBz	CH_3	-	E2	[65]

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
178	1*α*-benzoyloxy-2*α*,6*β*,8*α*,9*α*-tetraacetoxy-*β*-dihydroagarofuran	OBz	*α*-OAc	H	OAc	*α*-OAc	*α*-OAc	CH_3	-	E2	[65]
179	1*α*,6*β*,8*α*-triacetoxy-9*α*-benzoyloxy-2*α*-hydroxy-*β*-dihydroagarofuran	OAc	*α*-OH	H	OAc	*α*-OAc	*α*-OBz	CH_3	-	E2	[65]
180	(1*R*,2*S*,4*R*,5*S*,6*R*,7*R*,8*R*,9*S*,10*S*)-1,6-diacetoxy-8,9-dibenzoyloxy-2-h ydroxy-*β*-d ihydroagarofuran	OAc	*α*-OH	H	OAc	*α*-OBz	*α*-OBz	CH_3	-	E2	[65]
181	1*α*,6*β*,15-triacetoxy-8*α*-methylbutyroyloxy-9*α*-benzoyloxy-2*α*-hydroxy-*β*-dihydroagaro-furan	OAc	*α*-OH	H	OAc	*α*-OMeBut	*α*-OBz	CH_2OAc	-	E2	[65]
182	1*α*,6*β*,15-triacetoxy-8*α*,9*α*-dibenzoyloxy-2*α*-hydroxy-*β*-dihydroagarofuran	OAc	*α*-OH	H	OAc	*α*-OBz	*α*-OBz	CH_2OAc	-	E2	[65]
183	1*α*,6*β*,8*β*,15-tetracetoxy-2*α*-hydroxy-9*α*-benzoyloxy-*β*-dihydroagarofuran	OAc	*α*-OH	H	OAc	*β*-OAc	*α*-OBz	CH_2OAc	-	E2	[65]
184	Chiapens A	OH	*α*-OAc	H	OAc	*α*-OBz	*α*-OBz	CH_2OAc	-	E2	[66]
185	Chiapens B	OAc	*α*-OAc	H	OAc	*α*-OBz	*α*-OBz	CH_2OAc	-	E2	[66]
186	Chiapens C	OH	H	H	OAc	*α*-OBz	*α*-OBz	CH_2OAc	-	E2	[66]
187	Chiapens D	OAc	*α*-OAc	H	OBut	H	*α*-OBz	CH_2OAc	-	E2	[66]
188	Chiapens E	OAc	*α*-OAc	*β*-OAc	OAc	O	*α*-OBz	CH_2OAc	-	E2	[66]
189	1*α*,6*β*-diacetoxy-8*α*-hydroxy-9*β*-furoyloxy-*β*-agarofuran	OAc	H	H	OAc	*α*-OH	*β*-OFu	CH_3	-	E2	[67]
190	1*α*-acetoxy-6*β*,8*α*-dihydroxy-9*β*-furoyloxy-*β*-agarofuran	OAc	H	H	OH	*α*-OH	*β*-OFu	CH_3	-	E2	[67]
191	1*α*-benzoyloxy-2*α*,3*β*,6*β*,9*β*,14-pentaacetoxy-8-oxo-*β*-agarofuan	OBz	*α*-OAc	*β*-OAc	OBz	O	OAc	CH_2OAc	-	E2	[67]
192	1*α*-furoyloxy-2*α*,3*β*,6*β*,9*β*,14-pentaacetoxy-8-oxo-*β*-agarofuan	OFu	*α*-OAc	*β*-OAc	OFu	O	OAc	CH_2OAc	-	E2	[67]
193	Bilocularins A	OAc	H	H	OAc	*α*-OH	*α*-OBz	CH_2OAc	-	E2	[68]
194	Bilocularins B	OAc	H	H	OH	*α*-OAc	*α*-OBz	CH_2OAc	-	E2	[68]
195	Bilocularins C	OAc	H	H	OAc	O	*α*-OBz	CH_2OAc	-	E2	[68]
196	Bilocularins D	OHAc	*α*-OAc	H	OAc	CH_3	H	*β*-O*t*Cin	CH_2OBz	E1	[69]
197	Bilocularins E	OHAc	*α*-OAc	H	OAc	CH_3	H	*β*-O*t*Cin	CH_2O*t*Cin	E1	[69]
198	Bilocularins F	OHAc	*α*-OAc	H	OAc	CH_3	H	*β*-O*t*Cin	CH_2OH	E1	[69]
199	Bilocularins G	OAc	*α*-OAc	H	OAc	CH_3	H	*β*-O*t*Cin	CH_2OAc	E1	[69]
200	Bilocularins H	OAc	*α*-OH	H	OAc	CH_3	H	*β*-O*t*Cin	CH_2OH	E1	[69]
201	Bilocularins I	OAc	*α*-OH	H	ONic	CH_3	H	*β*-O*t*Cin	CH_3	E1	[69]
202	(1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9,10-trihydroxy-2,2,5*a*,9-tetramethyloctahydro-2*H*-3,9*a*-methanobenzo[*b*]oxepin-5-yl furan-3-carboxylate	OAc	H	H	OH	CH_3	*α*-OH	*β*-OFu	CH_3	E1	[70]
203	(1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9-dihydroxy-2,2,5*a*,9-tetramethyloctahydro-2*H*-3,9*a*-methanobenzo[*b*]oxepine-5,10-diylbis(furan-3-carboxylate)	OAc	H	H	OFu	CH_3	*α*-OH	*β*-OFu	CH_3	E1	[71]
204	(1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-9-hydroxy-2,2,5*a*,9-tetramethyloctahydro-2*H*-3,9*a*-methanobenzo[*b*]oxepine-5,10-diylbis(furan-3-carboxylate)	OAc	H	H	OFu	CH_3	H	*β*-OFu	CH_3	E1	[71]

2.3. Alkaloids

2.3.1. Sesquiterpene Pyridine Alkaloids

Among the naturally occurring nitrogen containing compounds, the pyridine alkaloids constitute an important group, and these are relatively rare natural products. The Celastraceae family is a rich source of sesquiterpene pyridine alkaloids. These compounds are endowed with a novel type of chemical diversity, and have complicated stereo-chemistries. They also possess a broad spectrum of biological activities, such as having immunosuppressive and anti-tumor properties. The vast majority of macrolide sesquiterpene pyridine alkaloids, from the genus *Maytenus*, are based on the [5,11-epoxy-5*β*,10*a*-cyclosilan-4(14)-ene] skeleton known as dihydro-*β*-agarofum. These compounds are characterized by a pyridine dicarboxylic acid macrocyclic bridge (such as evoninic, wilfordic and hydroxywilfordic acids), linked via two ester moieties at the C-3 and C-15 positions [65][76]. Many of these alkaloids have been isolated by organic chemists over recent years. Below we summarize their information, including the names of compounds, their original plant source as well as their structures.

The potent anti-feedant wilforine (**213**) was isolated from *M. rigida* [77]. Compounds emarginatines A–H (**214–221**) and emarginatinine (**222**) were obtained from *M. emarginata* and the leaves of *M. diversifolia*. [11][22][78][79]. Ebenifoline W-I (**223**), ebenifoline E-I (**224**) and ebenifoline E-II (**225**) were separated from the stem bark methanol extracts of *M. ebenifolia* Reiss [80]. Compounds aquifoliunines E-I-IV (**226–229**) have been obtained from the root barks of *M. aquiJolium*. [81][82], while ilicifoliunines A–B (**230–231**) and mayteine (**232**) were isolated from the root barks of *M. ilicifolia* [83]. Laevisines A (**233**) and B (**234**) have been separated from the $CHCl_3$:MeOH (9:1) extracts of the barks of *M. laevis* [84]. Compounds mekongensine (**235**), 7-*epi*-mekongensine (**236**), 1-*O*-benzoyl-1-deacetylmekongensine (**237**), 9′-deacetoxymekongensine (**238**), 1-*O*-benzoyl-1-deacetyl-9′-deacetoxymekongensine (**239**), 7-*epi*-euojaponine A (**240**), 2-

O-benzoyl-2-deacetylmayteine (**241**) and 7-*epi*-5-*O*-benzoyl-5-deacetylpericassine A (**242**) have been isolated from the roots of *M. mekongensis* [85]. The compound 5-benzoyl-5-deacetylwilforidine (**243**) was isolated from *M. buchananii* (Loes.) Wilczek. This appears to be the first sesquiterpene nicotinoyl alkaloid found which was based on hydroxywilforic acid with a benzoyl group at C-5 position [86]. Compounds putterines A (**244**) and B (**245**) have been separated from the roots of *M. putterlickoides* [76]. The compound 7-(acetyloxy)-O^{11}-benzoyl-$O^{2,11}$-deacetyl-7-deoxocathorinine (**246**) was isolated from the methanol extracts of the barks of the Colombian medicinal plant, *M. laevis* [52]. Chiapenines ES-I (**247**), ES-II (**248**), ES-III (**249**) and ES-IV (**250**) were isolated from the leaves of *M. chiapensis* [87]. Compound Ieiskine (**251**) was obtained from *M. jelskii* and *M. cuzcoina* [88]. Compounds O^9-benzoyl-O^9-deacetylevonine (**252**) and 8*β*-acetoxy-O^1-benzoyl- O^1-deacetyl-8-deoxoevonine (**253**) have been separated from the organic extracts of the roots of *M. Spinosa* [24]. Compounds 1*α*,2*α*,6*β*,8*β*,9*α*,15-hexacetoxy-4*β*-hydroxy-3*β*,13-[2′-(3-carboxybutyl)] nicotinicacid-dicarbo-lactone-*β*-dihydroagarofuran (**254**), 1*α*,2*α*,9*α*,15-tetracetoxy-4*β*,6*β*-dihydroxy-8-oxo,3*β*,13-[4′-(3-carboxybutyl)]nicotinicacid-dicarbolactone-*β*-dihydroagarofuran (**255**), 1*α*,2*α*,9*α*,15-tetracetoxy-4*β*,6*β*,8*β*-trihydroxy-3*β*,13-[4′-(3-carboxybutyl)] nicotinicacid-dicarbolactone-*β*-dihydroagarofuran (**256**) and 1*α*,2*α*,8*β*,9*α*,15-pent acetoxy-4*β*,6*β*-dihydroxy-3*β*,13-[4′-(3-carboxybutyl)] nicotinicaciddicarbolactne-*β*-dihydroagarofuran (**257**) were isolated from the leaves of *M. spinosa* [75]. Compounds 4-deoxyalatamine (**258**), 1-*O*-benzoyl-1-deacetyl-4-deoxy-alatamine (**259**), 1,2-*O*-dibenzoyl-1,2-deacetyl-4-deoxyalatamine (**260**) and 4-deoxyisowilfordine (**261**) were obtained from an ethyl acetate extract of *M. oblongata* stems [31] (**Table 6** and **Figure 6**).

No.	Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Type	Ref.
205	(1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6-acetoxy-10-[benzoyl(methyl)amino]-1-hydroxy-2,2,5,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[b]oxepin-5-yl nicotinate-3-carboxylate	OAc	H	H	OBz	CH_3	*β*-OFu	CH_3		E1	[71]
206	2*β*,6*β*-diacetoxy-1*α*,8*β*-dibenzoyl-3*β*-hydroxy-dihydro-*β*-agarofuran	*α*-OBz	*β*-OAc	*β*-OH	H	*β*-CH_3				E3	[72]
207	1*α*,2*α*,6*β*,8*α*-tetraacetoxy-9*β*-benzoyl-15-hydroxy-dihydro-*β*-agarofuran	*α*-OAc	*α*-OAc	H	*α*-OAc	*α*-CH_2OH				E4	[72]
208	1*α*,2*α*,6*β*,8*α*,15-pentaacetoxy-9*β*-benzoyl-dihydro-*β*-agarofuran	*α*-OAc	*α*-OAc	H	*α*-OAc	*α*-CH_2OAc				E3	[72]
209	1*β*-acetoxy-9*α*-benzoyloxy-2*β*,6*α*-dinicotinoyloxy-*β*-dihydro agarofuran(heterophylline)									E4	[73]
210	Boarioside	-	-	-	-	-	-	-	-	E5	[74]
211	4-deacetyl-10[65]-dihydrobotrydial									E6	[75]
212	4*β*-acetoxy-9*β*,10*β*,15*α*-trihydroxyl-robotrydial									E7	[75]

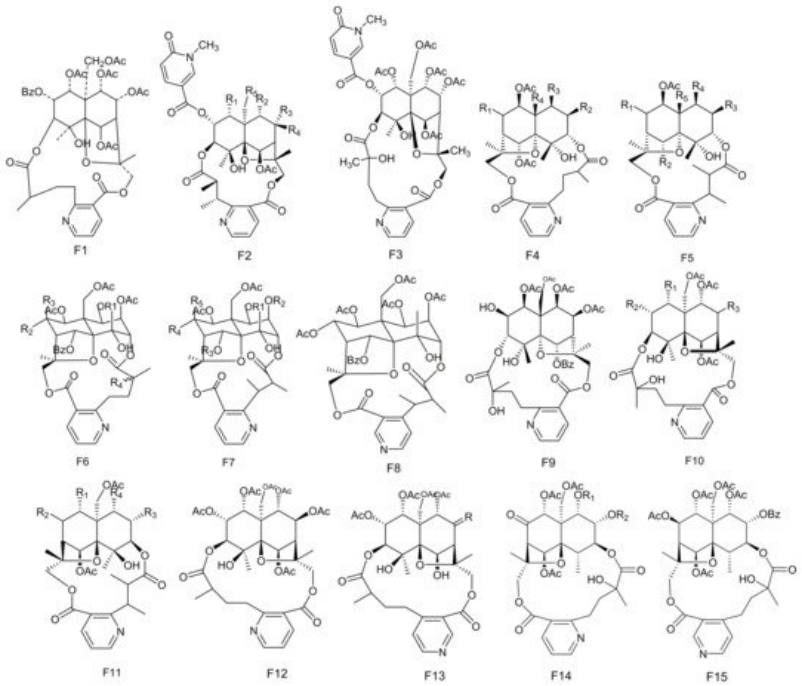
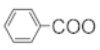
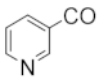
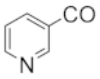


Figure 6. Fifteen types (F1–F15) of sesquiterpene pyridine alkaloids skeletons.

Table 6. The sesquiterpene pyridine alkaloids isolated from *Maytenus*.

No.	Name	R_1	R_2	R_3	R_4	R_5	Type	Ref.
213	Wilforine	-	-	-	-	-	F1	[77]
214	Emarginatine-A	OAc	OAc	OAc	H	OAc	F2	[78]
215	Emarginatine-B	OAc	Benzoate	H	OAc	OAc	F2	[78]
216	Emarginatine-C	OAc	OH	OAc	H	OAc	F2	[79]
217	Emarginatine-D	OA	OAc	OAc	H	OAc	F2	[79]
218	Emarginatine-E	OH	OH	H	OAc	OAc	F2	[79]
219	Emarginatine-F		OAc	H	OH	OAc	F2	[11]
220	Emarginatine-G	$CH_3CH=CCH_3OO$	OAc	OAc	H	OAc	F2	[11]
221	Emarginatine-H	OAc	OAc	OAc	H	OH	F2	[22]
222	Emarginatinine	-	-	-	-	-	F3	[79]

No.	Name	R_1	R_2	R_3	R_4	R_5	Type	Ref.
223	Ebenifoline W-I	*β*-OAc	OBz	OBz	OAc	-	F4	[80]
224	Ebenifoline E-I	*β*-OAc	OAc	OH	OBz	OAc	F5	[80]
225	Ebenifoline E-II	*β*-OAc	OBz	OAc	OBz	OAc	F5	[80]
226	Aquifoliunine E-I	*α*-OBz	OAc	OAc	OAc	CH_2OAc	F5	[81]
227	Aquifoliunine E-II	*α*-OH	OAc	OH	OAc	CH_2OAc	F5	[81]
228	Aquifoliunine E-III	*α*-OH	OAc	OAc	OAc	CH_2OAc	F5	[82]
229	Aquifoliunine E-IV	*α*-ONic	OAc	OAc	OAc	CH_2OAc	F5	[82]
230	Ilicifoliunines A	*α*-OBz	OH	OAc	OAc	CH_2OAc	F5	[83]
231	Ilicifoliunines B	*α*-OBz	OAc	OAc	CH_2OAc	-	F4	[83]
232	Mayteine	*β*-OAc	OAc	OAc	OBz	CH_2OAc	F5	[83]
233	Laevisines A	*β*-OAc	OAc	OAc	$OCOC(CH_3)=CHCH_3$	CH_2OAc	F5	[84]
234	Laevisines B	β-OAc	OAc	ONic	CH_2OAc	-	F4	[84]
235	Mekongensine	Ac	H	OAc	OAc	-	F6	[85]
236	7-*epi*-mekongensine	Ac	OAc	H	OAc	-	F6	[85]
237	1-*O*-benzoyl-1-deacetylmekongensine	Bz	H	OAc	OAc	-	F6	[85]
238	9′-deacetoxymekongensine	Ac	H	OAc	H	-	F6	[85]
239	1-*O*-benzoyl-1-deacetyl-9′-deacetoxymekongensine	Bz	H	OAc	H	-	F6	[85]
240	7-*epi*-euojaponine	Bz	Ac	H	OAc	H	F7	[85]
241	2-*O*-benzoyl-2-deacetylmayteine	Bz	Bz	Ac	H	OAc	F7	[85]
242	7-*epi*-5-*O*-benzoyl-5-deacetylperitassine A	-	-	-	-	-	F8	[85]
243	5-benzoyl-5-deacetylwilforidine	-	-	-	-	-	F9	[86]
244	Putterines A		OAc	$COOCH_3$	$COOCH_3$	CH_2OAc	F5	[76]
245	Putterines B		OAc	$COOCH(CH_3)_2$	$COOCH_3$	CH_2OAc	F5	[76]
246	7-(acetyloxy)-O^{11}-benzoyl-$O^{2,11}$-deacetyl-7-deoxoevonine	*β*-OAc	OAc	OH	OAc	CH2OBz	F5	[52]
247	Chiapenines ES-I	OBz	OBz	*α*-OAc	-	-	F10	[87]
248	Chiapenines ES-II	OBz	OBz	=O	-	-	F10	[87]
249	Chiapenines ES-III	OBz	OH	=O	-	-	F10	[87]
250	Chiapenines ES-IV	OAc	OH	=O	-	-	F10	[87]
251	Jelskiine	OiBut	*α*-OAc	OH	OAc	-	F11	[88]
252	O^9-benzoyl-O^9-deacetylevonine	OBz	=O	OAc	OAc	-	F11	[24]
253	8*β*-acetoxy-O^1-benzoyl- O^1-deacetyl-8-deoxoevonine	OAc	*β*-OAc	OAc	OBz	-	F11	[24]
254	1*α*,2*α*,6*β*,8*β*,9*α*,15-hexacetoxy-4*β*-hydroxy-3*β*,13-[2′-(3-carboxybutyl)]nicotinicacid-dicarbo-lactone-*β*-dihydroagarofuran	-	-	-	-	-	F12	[65]

No.	Name	R_1	R_2	R_3	R_4	R_5	Type	Ref.
255	1α,2α,9α,15-tetracetoxy-4β,6β-dihydroxy-8-oxo,3β,13-[4′-(3-carboxybutyl)]nicotinicacid-dicarbolactone-β-dihydroagarofuran	=O	-	-	-	-	F13	[65]
256	1α,2α,9α,15-tetracetoxy-4β,6β,8β-trihydroxy-3β,13-[4′-(3-carboxybutyl)]nicotinicacid-dicarbolactone-β-dihydroagarofuran	β-OH	-	-	-	-	F13	[65]
257	1α,2α,8β,9α,15-pentacetoxy-4β,6β-dihydroxy-3β,13-[4′-(3-carboxybutyl)]nicotinicaciddicarbolactne-β-dihydroagarofuran	OAc	-	-	-	-	F13	[65]
258	4-deoxyalatamine	OAc	OAc	-	-	-	F14	[31]
259	1-*O*-benzoyl-1-deacetyl-4-deoxy-alatamine	OBz	OAc	-	-	-	F14	[31]
260	1,2-*O*-dibenzoyl-1,2-deacetyl-4-deoxyalatamine	OBz	OBz	-	-	-	F14	[31]
261	4-deoxyisowilfordine	-	-	-	-	-	F15	[31]

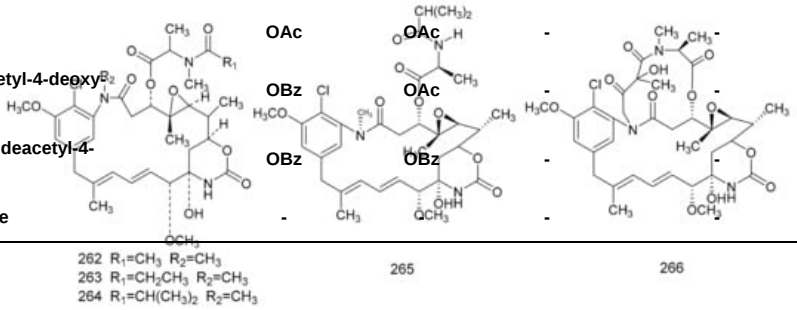


Figure 7. The chemical structures of *maytansinoids*, isolated from *Maytenus*.

2.3.2. Maytansinoids

In 1972, Kupchan et al. [7] found a macrolide alkaloid, maytansine (**262**), which was a natural product that had anti-tumor activities, and this was first isolated from *M. serrata*. Compound **262** is an anti-tumor agent with a novel structure, and, therefore, is of great clinical interest. Subsequently, maytansine (**262**), maytanprine (**263**) and maytanbutine (**264**) were isolated from *M. buchananii* [89]. Larson et al. [90] also isolated two new maytansinoid compounds, 2′-*N*-desmethylmaytanbutine (**265**) and maytanbicyclinol (**266**) from *M. buchananii* (**Figure 7**).

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