CHEMICAL REVIEWS

Review

Chemical and Pharmacological Research of the Plants in Genus *Euphorbia*

Qing-Wen Shi, Xiao-Hui Su, and Hiromasa Kiyota

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Chemical and Pharmacological Research of the Plants in Genus *Euphorbia*

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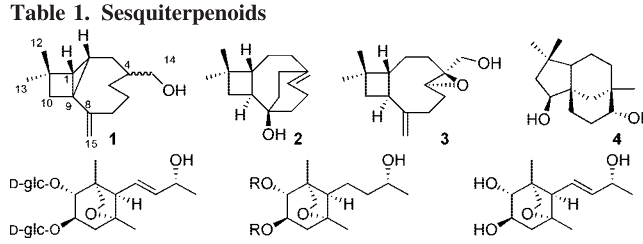
Received August 14, 2007

Contents

Figure 1. Flower of *Euphorbia pekinensis* Rupr.

Table 1. Sesquiterpenoids



no.	name	plant	ref
1	euphanginol	*E. wangii*	10
2	cyclocaryophylla-4-en-8-ol	*E. wangii*	10
3	4β,5α-epoxy-4,5-dihydrocaryophyllen-14-ol	*E. wangii*	10
4	clovandiol	*E. wangii*	10
5	euphorbioside A	*E. resinifera*	11
6	euphorbioside B	*E. resinifera*	11
7	deglucosyl euphorbioside A	*E. resinifera*	11

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Xiao-Hui Su (b. 1983 in Qinhuangdao, Hebei Province). She got her Bachelor and Master degrees from School of Pharmaceutical Sciences, Hebei Medical University in 2005 and 2008. Her master thesis is studies on the antitumour compounents of *Euphorbia lathyris* seeds and flowers of *Inula japonica*.

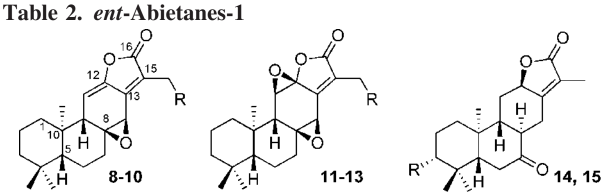
Hiromasa Kiyota (b. 1966 in Sendai, Japan), Associate Professor of Biooganic Chemistry at Tohoku University, Japan. He received his B. S. degree (1989, soil science, Prof. Hidenori Wada) and M. S. degree (1991, organic chemistry, Prof. Kenji Mori and Associate Prof. Takeshi Kitahara) from the University of Tokyo. In 1991 he assumed the position of Assistant Professor at Prof. K. Mori's Laboratory, moved to Prof. Takayuki Oritani's Laboratory in 1994, and he was promoted to Associate Professor (Prof. Shigefumi Kuwahara) in 2002. In 1995 he received his PhD from the University of Tokyo (Prof. Kenji Mori and Prof. Takeshi Kitahara) about the synthesis of optically active insect pheromones. He joined the research group of Prof. Steven V. Ley at Cambridge University, U.K. as Visiting Academic (2001−2002). In 2003 he received The Japan Bioscience, Biotechnology and Agrochemistry Society Award for the Encouragement of Young Scientists. His research interests extend over a wide range of natural product chemistry, especially on the synthesis of biologically active compounds such as antibiotics, phytotoxins, plant hormones, insect pheromones, marine products, perfumery, etc.

1. Introduction

The genus *Euphorbia* is the largest in the spurge family, comprising more than 2000 species (Figure 1).[1] Some species of the genus *Euphorbia* have been used as medicinal plants for the treatment of skin diseases, gonorrhea, migraine, and intestinal parasites and as wart cures.[2] The researched parts of the *Euphorbia* species include roots, seeds, latex, lactiferous tubes, stem wood, stem barks, leaves, and whole plants. Plants in the family Euphorbiaceae are well known for the chemical diversity of their isoprenoid constituents.[3] Diterpenoids are the majority of the genus with many different core frameworks such as jatrophanes, lathyranes, viglianes, ingenanes, myrsinols, etc. The triterpene alcohols found in the latex of *Euphorbia* species have been used as chemotaxonomic markers.[4,5] In addition, sesquiterpenoids, phloracetophenones, cerebrosides, glycerols, flavonoids, and steroids were also obtained. The compounds isolated from genus *Euphorbia* and extracts perform many different activities, including antiproliferation, modulability of multidrug resistance, cytotoxic activity, antimicrobial and antiinflammatory activity, etc. Biological activities including skin irritant, tumor promotion, and proinflammatory properties are attributed to the presence of specific classes of macro- and polycyclic diterpenes.[6−9]

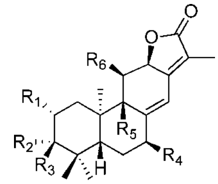
In this review article, we will summarize the phytochemical progress and list all of the compounds isolated from the

Table 2. ***ent*****-Abietanes-1**



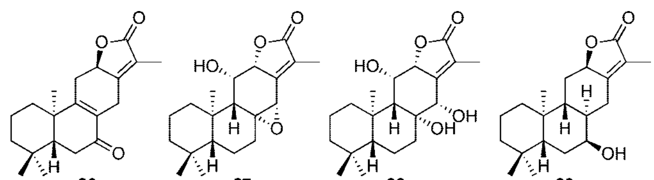
no.	name	R	plant	ref
8	17-acetoxyjolkinolide A	OAc	*E. fischeriana*	13
9	jolkinolide A	H	*E. fischeriana*	14
			E. sessiliflora	15
			E. portulacoides	16
10	17-hydroxyjolkinolide A	OH	*E. fischeriana*	13
			E. acaulis	17
			E. caudicifolia	18
			E. portulacoides	16
			E. sessiliflora	15
11	jolkinolide B	H	*E. fischeriana*	14
			E. sessiliflora	15
			E. seguieriana	19
			E.ebracteolata	20
			E. portulacoides	16
12	17-hydroxyjolkinolide B	OH	*E. fischeriana*	14
13	17-acetoxyjolkinolide B	OAc	*E.fischeriana*	21
14	8α,14-dihydro-7-oxojolkinolide E	H	*E. characias*	22
15	8α,14-dihydro-7-oxohelioscopinolide A	OH	*E. semiperfoliata*	23
			E. characias	22

Table 3. *ent*-Abietanes-2

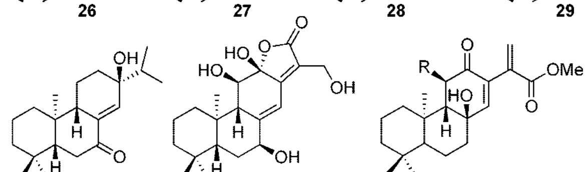


no.	name	R1	R2	R3	R4	R5	R6	plant	ref
16	7*β*-hydroxy-*ent*-abieta-8(14),13(15)-dien-12α,16-olide	H	H	H	OH	H	H	*E. seguieriana*	19
17	7*β*,9*β*-dihydroxy-*ent*-abieta-8(14),13(15)-dien-12α,16-olide	H	H	H	OH	OH	H	*E. seguieriana*	19
18	-*ent*-11*β*-hydroxyabieta-8(14),13(15)-dien-12*β*,16-olide	H	H	H	H	H	OH	*E. fischeriana*	13
								E. fidjiana	24
19	jolkinolide E	H	H	H	H	H	H	*E. helioscopia*	25
								E. characias	22
20	helioscopinolide A	H	OH	H	H	H	H	*E. characias*	22
								E. helioscopia	25
								E. pubescens	26
								E. semiperfoliata	23
21	helioscopinolide B	H	H	OH	H	H	H	*E. characias*	22
								E. helioscopia	25
								E. pubescens	26
								E. semiperfoliata	23
22	2α-hydroxyhelioscopinolide B	OH	OH	H	H	H	H	*E. helioscopia*	12
23	helioscopinolide C	=O	OH	H	H	H	H	*E. helioscopia*	25
24	helioscopinolide D	H	=O	=O	H	OH	H	*E. calyptrate*	27
25	helioscopinolide E	H	=O	=O	H	H	H	*E. calyptrate*	27

Table 4. *ent*-Abietanes-3



26 **27** **28** **29**



30 **31** **32, 33**

no.	name	R	plant	ref
26	7-oxo-*ent*-abieta-8,13(15)-dien-12α,l6-olide	–	*E. seguieriana*	19
27	ebracteolatanolide A	–	*E.ebracteolata*	20
28	ebracteolatanolide B	–	*E.ebracteolata*	20
29	8α,14-dihydro-7*β*-hydroxyjolkinolide E	–	*E. terracina*	28
30	13*β*-hydroxy-*ent*-abiet-8(14)-en-7-one	–	*E.fischeriana*	21
31	langduin B: 7*β*,11*β*,12*β*,17-tetrahydroxy-*ent*-abieta-8(14),13(15)-dien-16,12α-olide	–	*E. fischeriana*	13
32	methyl 8*β*-hydroxy-12-oxo-*ent*-abieta-13,15(17)-dien-16-oate	H	*E. portulacoides*	16
33	methyl 8*β*,11*β*-dihydroxy-12-oxo-*ent*-abieta-13,15(17)-dien-16-oate	OH	*E. portulacoides*	16

genus *Euphorbia* over the past few decades. Also included are the biological activities of compounds isolated in recent years and parts structure–activity relationships.

2. Chemical Constituents

2.1. Sesquiterpenoids (Table 1)

In 1997, Shi et al. reported the isolation of a new (**1**) and three known (**2**–**4**) sesquiterpenoids from *E. wangii*.[10] This is the first investigation on sesquiterpenoids from the genus *Euphorbia*. In 2002, Fattorusso et al. isolated two novel bisnorsesquiterpene glycosides, euphorbiosides A (**5**) and B (**6**), as well as the aglycone of **5** (compound **7**) from more polar fractions of *E. resinifera*.[11] In 2006, Zhang et al. isolated two known nor-sesquiterpenoids, 4,5-dihydroblumenol A and aglycone of icariside B2, from *E. helioscopia*.[12]

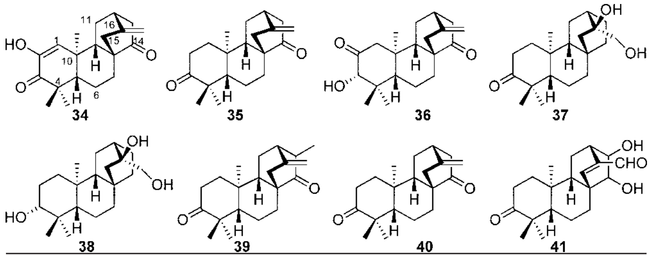
2.2. Higher Diterpenoids

2.2.1. ent-Abietanes, ent-Atisanes, ent-Kauranes, ent-Isopimaranes, and ent-Pimaranes (Tables 1–9)

Polycyclic diterpenoids with a common 6/6/6-tricyclic ring are also major constituents of *Euphorbia*. Higher diterpenoids originated from geranylgeranyl diphosphate by "concertina-like" cyclization, *ent*-abietanes, *ent*-atisanes, *ent*-kauranes, *ent*-isopimaranes, and *ent*-pimaranes, are introduced as follows.

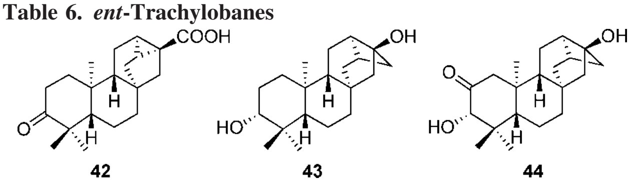
The *ent*-abietanes from this species usualy contain fourth α,*β*-unsaturated *γ*-lactone ring. 2α-Hydroxyhelioscopinolide

Table 5. *ent*-Atisanes



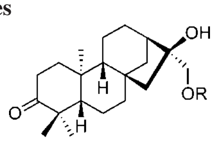
no.	name	plant	ref
34	*ent*-2-hydroxyatisa-1,16(17)-diene-3,14-dione	*E. characias*	22
35	*ent*-atis-16(17)-ene-3,14-dione	*E. characias*	22
		E. fidjiana	29
36	*ent*-3α-hydroxyatis-16(17)-ene-2,14-dione	*E. characias*	22
37	*ent*-16α,17-dihydroxyatisan-3-one	*E. quinquecostata*	30
		E. fidjiana	29
38	*ent*-atisane-3β,16α,17-triol	*E. quinquecostata*	30
		E. fidjiana	31
39	*ent*-(13 *R*)-hydroxyatis-16(17)-ene-3,4-dione	*E. fidjana*	32
40	*ent*-atis-16(17)-ene-3,4-dione	*E. fidjana*	32
41	*ent*-(13 *R*,14 *R*)-dihydroxyatis-15-ene-15,17-dione	*E. fidjana*	32

Table 6. *ent*-Trachylobanes



no.	name	plant	ref
42	*ent*-3-oxo-trachyloban-17-oic acid	*E. wallichii*	33
43	wallichanol A	*E. wallichii*	33
44	wallichanol B	*E. wallichii*	33

Table 7. *ent*-Kauranes



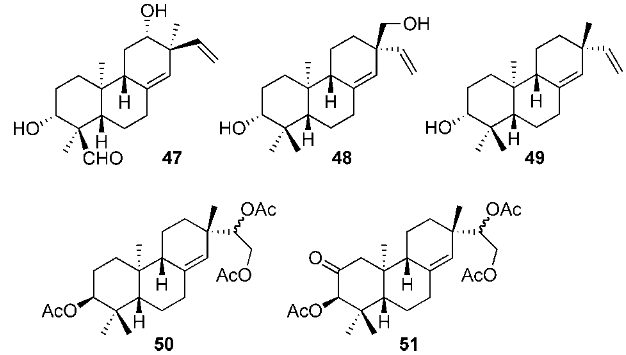
no.	name	R	plant	ref
45	16β,17-dihydroxy-*ent*-kauran-3-one	H	*E. characias*	22
			E. portulacoides	16
			E. sieboldiana	34
			E. wallichii	35
46	17-acetoxy-16β-hydroxy-*ent*-kauran-3-one	Ac	*E. portulacoides*	16

B (**22**), which was reported as an intermediate in the course of structure elucidation of helioscopinolide C (**23**), was isolated from natural sources for the first time in 2006 by Zhang et al.[12] The occurrence of *ent*-atisanes in plants from the genus *Euphorbia* is very rare and, apart from *E. fidjiana*, has so far been documented only in the roots of the Indian species *E. acaulis* Roxb.[37]

2.2.2. Other Diterpenoids

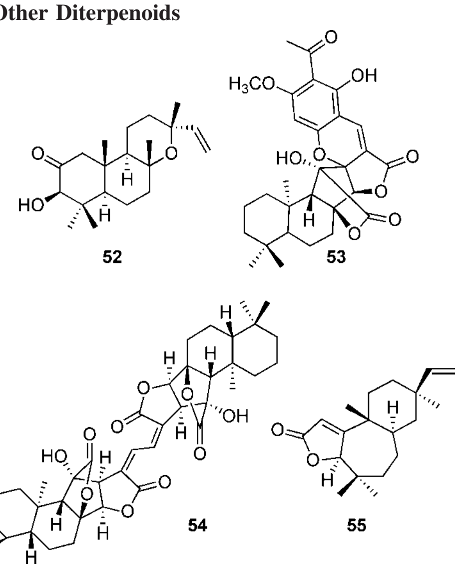
In 1997, a manoyloxide derivative, 3β-hydroxy-2-oxomanoyloxide (**52**) was isolated from *E. segetalis* by Jakupovic et al.[38] Langduin C (**53**), a novel dimeric diterpenoid, was isolated from the roots of *E. fischeriana*.[40] In 1999, fischeria A (**55**), a novel norditerpene lactone from *E. fischeriana*, was isolated from the rhizomes of *E. fischeriana* Steud.[41]

Table 8. *ent*-Isopimaranes and *ent*-Pimaranes



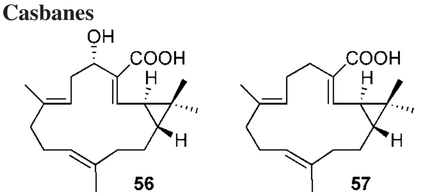
no.	name	plant	ref
47	3α,12α-dihydroxy-*ent*-8(14),15-isopimaradien-18-al	*E. quinquecostata*	36
48	*ent*-pimara-8(14),15-diene-3α,17-diol	*E. fischeriana*	21
49	*ent*-pimara-8(14),15-dien-3α-ol	*E. characias*	22
50	3β,15,16-triacetoxy-*ent*-pimar-8(14)-ene	*E. characias*	22
51	3β,15,16-triacetoxy-*ent*-pimar-8(14)-en-2-one	*E. characias*	22

Table 9. Other Diterpenoids



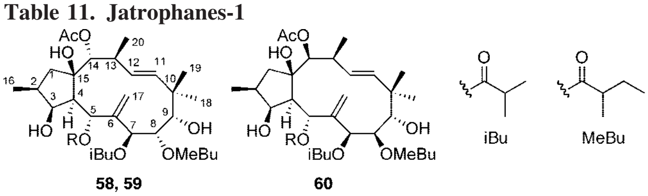
no.	name	plant	ref
52	3β-hydroxy-2-oxomanoyloxide	*E. segetalis*	38
53	langduin D	*E. fischeriana*	39
54	langduin C	*E. fischeriana*	40
55	fischeria A	*E. fischeriana*	41

Table 10. Casbanes



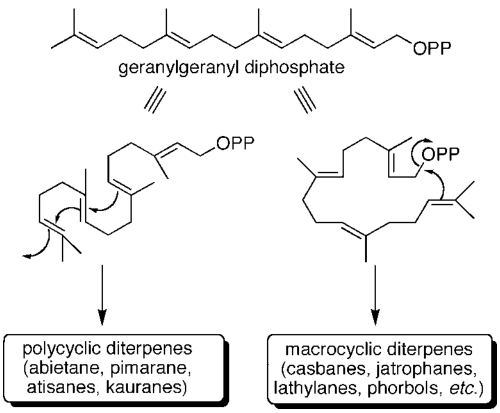
no.	name	plant	ref
56	yuexiandajisu A	*E. ebracteolata*	42
57	yuexiandajisu B	*E. ebracteolata*	42

Table 11. Jatrophanes-1

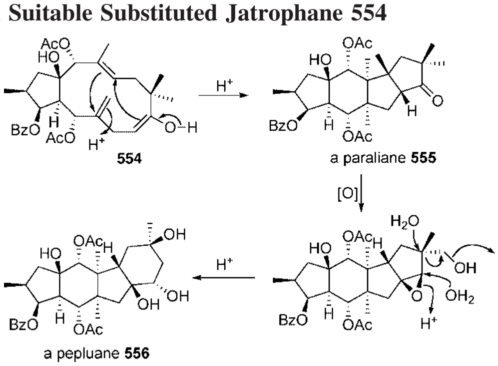


no.	name	R	plant	ref
58	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *S*,9 *S*,13 *S*,14 *R*,15 *R*)-14-acetoxy-7-isobutyryloxy-5,8-bis(2-methylbutanoyloxy)jatropha-6(17),11 *E*-diene-3,9,15-triol	iBu	*E. terracina*	43
59	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *S*,9 *S*,13 *S*,14 *R*,15 *R*)-14-acetoxy-5,7-diisobutyryloxy-8-(2-methylbutanoyloxy)jatropha-6(17),11 *E*-diene-3,9,15-triol	MeBu	*E. terracina*	43
60	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *R*,9 *S*,13 *S*,14 *S*,15 *R*)-14-acetoxy-5,7-diisobutyryloxy-8-(2-methylbutanoyloxy)jatropha-6(17),11 *E*-diene-3,9,15-triol	–	*E. segetalis*	38

Scheme 1. Possible Biogenetic Route from Geranylgeranyl Diphosphate to Polycyclic and Macrocyclic Diterpenoids



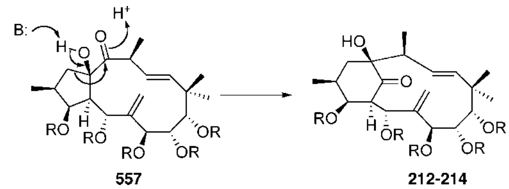
Scheme 2. Proposed Biogenesis of a Pepluane 556 Starting from a Suitable Substituted Jatrophane 554



2.3. Lower Diterpenoids

Considerable attention has been paid to the macrocyclic diterpenoids derived from cembrane cation because of their high chemical diversity and therapeutically relevant bioactivity. "Euphorbiaceae diterpenoids" include casbanes, jatrophanes, lathyranes, myrsinanes, tiglianes, ingenanes, segetanes, paralianes, pepluanes, and euphoractines as shown below.

Scheme 3. Pinacol-Type Rearrangement of a Jatrophane to 1(15→14) *Abeo*jatrophane (212−214)



2.3.1. Casbanes (Table 10)

Two bicyclic diterpenoids with a casbane skeleton (**56** and **57**) were isolated from *E. ebracteolata*.[42]

2.3.2. Jatrophanes (Tables 11– 28)

Euphorbiacea is a great rich source of jatrophane and the related diterpenoids. Jatrophanes with various oxygenation stages and stereoisomers are listed in the tables. These compounds are usually substituted with various acyl groups, such as acetyl, propanoyl, butanoyl, isobutyryl, benzoyl, tigloyl, nicotinoyl, angeloyl, etc., and are sometimes called jatrophane polyesters. Corea et al. carried out a molecular mechanic and dynamics calculation on amygdaloidins A−L (**120**−**131**).[56] The data obtained gave further information on the *endo*- and *exo*-type major conformations for the jatrophane diterpenoids. On the other hand, the stereochemistry of hemiacetal type jatrophane, esulatin C (**187**), at C-7, C-8, C-9, C-11, and C-13 could not be determined on the basis of NOESY correlations because of the high flexibility of this part of the molecule.[58] Compound **191** is the only jatrophane with 12,15-epoxy ring.[68] 17-Bishomojatrophanes forming 6- or 8-membered lactone ring teracinolides (**192**−**210**) and salicinolide (**211**) were found.[28,38,73−76] Salicifoline (**215**) is the first representative of a new type of tricyclic diterpenoids involving a novel 5/8/8 fused ring system, that is, 12,17-cyclojatrophane.[76] Euphosalicin (**216**) also contains a new 9(10→18) *abeo*jatrophane skeleton.[63]

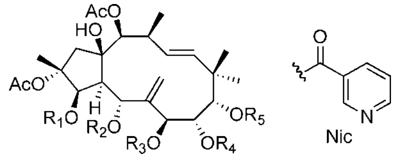
2.3.3. Lathyranes (Tables 29−33)

Lathyranes with a 5/11/3-membered ring are also very common in *Euphorbia* species. Several compounds are substituted with methoxy group (Tables 29 and 31). Phenyacetyl and methoxyphenylacetyl groups are rather diagnostic to lathyranes. Lathyranoic acid A (**260**) is the first seco-lathyrane diterpenoid in nature from *E. lathyris*.[91] Lathyranone A (**261**) is a novel 1(15→14) *abeo*lathyrane compound also isolated from *E. lathyris* (section 3).[91]

2.3.4. Myrsinanes, Cyclomyrsinanes, and Premyrcinanes (Tables 34−43)

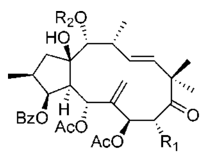
Myrsinanes and cyclomyrsinanes are derived from lathyranes via premyrsinanes (section 3). In addition to the normal myrsinanes (6,12-cyclojatrophanes) with a 5/7/5-ring carbon framework, compounds with a hemiacetal ring, a 13,17-epoxy ring, or a 10,13-epoxy ring are tabulated in Tables 34–39. the stereochemistry of all the frameworks and substituents are the same in myrsinanes. 9-Bishomomyrsinane **299** contains a δ-lactone ring.[107] The configuration of 12-position of eufobeotol (**306**) is reversed.[111] All the cyclomyrsinanes **300**−**305** have a 12,17-epoxy ring. Premyrsinanes **319**−**323** forms a rare acetyl hemiacetal moiety.

Table 12. Jatrophanes-2

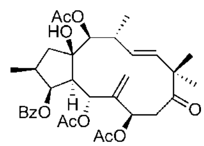


no.	name	R_1	R_2	R_3	R_4	R_5	plant	ref
61	2,5,14-triacetoxy-3-benzoyloxy-7-isobutyryloxy-9-nicotinoyloxy jatropha-6(17),11 *E*-diene-8,15-diol	Bz	Ac	iBu	H	Nic	*E. peplus*	44
62	2,5,7,8,9,14-hexaacetoxy-3-benzoyloxyjatropha-6(17),11 *E*-dien-15-ol	Bz	Ac	Ac	Ac	Ac	*E. peplus*	44
63	2,5,9,14-tetraacetoxy-3- benzoyloxy-7-isobutyryloxyjatropha-6(17),11 *E*-diene-8,15-diol	Bz	Ac	iBu	H	Ac	*E. peplus*	44
64	2,5,7,14-tetraacetoxy-3-benzoyloxy-9-nicotinoyloxyjatropha-6(17),11 *E*-diene-8,15-diol	Bz	Ac	Ac	H	Nic	*E. peplus*	44
65	2,5,7,9,14-pentaacetoxy-3-benzoyloxyjatropha-6(17),11 *E*-diene-8,15-diol	Bz	Ac	Ac	H	Ac	*E. peplus*	44
66	pepluanin A	Bz	Ac	Ac	Ac	Nic	*E. peplus*	45
67	pepluanin B	Bz	Ac	MeBu	H	Nic	*E. peplus*	45
68	pepluanin C	Ac	iBu	Bz	Ac	Ac	*E. peplus*	45

Table 13. Jatrophanes-3



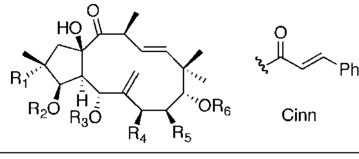
69-74



75

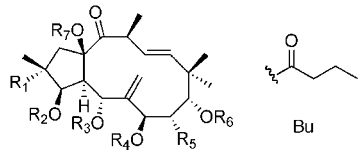
no.	name	R_1	R_2	plant	ref
69	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *R**,13 *R**,14 *R**,15 *R**)-5,7,8,14-tetraacetoxy-3-benzoyloxy-15-hydroxyjatropha-6(17),11 *E*-dien-9-one	OAc	Ac	*E. semiperfoliata*	23
70	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *R**,13 *R**,14 *R**,15 *R**)-5,7,14-triacetoxy-3-benzoyloxy-15-hydroxy-8-isobutyryloxyjatropha-6(17),11 *E*-dien-9-one	OiBu	Ac	*E. semiperfoliata*	23
71	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *R**,13 *R**,14 *R**,15 *R**)-5,7-diacetoxy-3-benzoyloxy-8,14,15-trihydroxyojatropha-6(17),11 *E*-dien-9-one	OH	H	*E. semiperfoliata*	23
72	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *R**,13 *R**,14 *R**,15 *R**)-5,7,8-triacetoxy-3-benzoyloxy-14,15-dihydroxyjatropha-6(17),11 *E*-dien-9-one	OAc	H	*E. semiperfoliata*	23
73	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *R**,13 *R**,14 *R**,15 *R**)-5,7,14-triacetoxy-3-benzoyloxy-8,15-dihydroxyjatropha-6(17),11 *E*-dien-9-one	OH	Ac	*E. semiperfoliata*	23
74	(2 *S**,3 *S**,4 *R**,5 *R**,7 *R**,13 *R**,14 *R**,15 *R**)-5,7,14-triacetoxy-3-benzoyloxy-15-hydroxyjatropha-6(17),11 *E*-dien-9-one	H	Ac	*E. semiperfoliata* *E. hyberna* subsp. *insularis*	23 46
75	(2 *S**,3 *S**,4 *R**,5 *R**,7 *R**,13 *R**,14 *S**,15 *R**)-5,7,14-triacetoxy-3-benzoyloxy-15-hydroxyjatropha-6(17),11 *E*-dien-9-one	–	–	*E. semiperfoliata*	47

Table 14. Jatrophanes-4



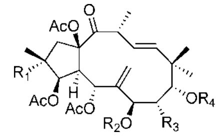
no.	name	R_1	R_2	R_3	R_4	R_5	R_6	plant	ref
76	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *S**,9 *S**,l3 *S**,15 *R**)-3,9,15-trihydroxy-5,7,8-triisobutyryloxyjatropha-6(17),11 *E*-dien-14-one	H	H	iBu	OiBu	OiBu	H	*E. segetalis*	38
77	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *S**,9 *S**,l3 *S**,15 *R**)-3,9,15-trihydroxy-7-isobutyryloxy-5,8-bis(2-methylbutanoyloxy)jatropha-6(17),11 *E*-dien-14-one	H	H	MeBu	OiBu	OMeBu	H	*E. segetalis*	38
78	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *S**,9 *S**,l3 *S**,15 *R**)-3,9,15-trihydroxy-5,7-diisobutyryloxy-8-(2-methylbutanoyloxy)jatropha-6(17),11 *E*-dien-14-one	H	H	iBu	OiBu	OMeBu	H	*E. segetalis*	38
79	1,5,8,9-tetraacetoxy-2-benzoyloxyacetoxy-7-isobutyryloxyjatropha-6(17),11E-dien-14-one	OAc	BzOAc	Ac	OiBu	OAc	Ac	*E. segetalis*	38
80	5-acetoxy-3-benzoyloxy-9-cinnamoyloxy-15-hydroxyjatropha-6(17),11E-dien-14-one	H	Bz	Ac	H	H	Cinn	*E. segetalis*	38
81	5-acetoxy-3,9-dicinnamoyloxy-15-hydroxyjatropha-6(17),11E-dien-14-one	H	Cinn	Ac	H	H	Cinn	*E. segetalis*	38

Table 15. Jatrphanes-5



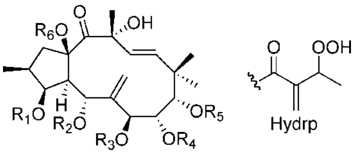
no.	name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	plant	ref
82	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-5,7,8-tris(2-methylbutanoyloxy)-3,9,15-trihydroxyjatropha-6(17),11-dien-14-one	H	H	MeBu	OMeBu	OMeBu	H	H	*E. terracina*	43
83	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-3,9,15-trihydroxy-5,7,8-triisobutyryloxyjatropha-6(17),11-dien-14-one	H	H	iBu	OiBu	OiBu	H	H	*E. terracina*	43
84	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*-3,9,15-trihydroxy-7-isobutyryloxy-5,8-bis(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	H	H	MeBu	OiBu	OMeBu	H	H	*E. terracina*	43
85	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-3,9,15-trihydroxy-5,7-diisobutyryloxy-8-(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	H	H	iBu	OiBu	OMeBu	H	H	*E. terracina*	43
86	pepluanin D	H	Ac	Ac	Ac	H	Ac	Ac	*E. peplus*	45
87	pepluanin E	OAc	Bz	Ac	iBu	OH	Nic	H	*E. peplus*	45
88	2α,3*β*,5α,8α,9α,15*β*-hexaacetoxy-7*β*-benzoyloxyjatropha-6(17),11*E*-dien-14-one	OAc	Ac	Ac	Bz	OAc	Ac	Ac	*E. turczaninowii*	48
89	3*β*,5α,8α,9α,15*β*-pentaacetoxy-7*β*-benzoyloxyjatropha-6(17),11*E*-dien-14-one	H	Ac	Ac	Bz	OAc	Ac	Ac	*E. turczaninowii*	48
90	3*β*,5α,7*β*,8α,9α,15*β*-hexaacetoxy-2α-benzoyloxyjatropha-6(17),11*E*-dien-14-one	OBz	Ac	Ac	OAc	OAc	Ac	Ac	*E. turczaninowii*	48
91	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *S*,9 *S*,13 *S*,15 *R*)-3-acetoxy-5,9,15-trihydroxy-7-isobutyryloxy-8-(2-methylbutanoyloxy)-jatropha-6(17),11 *E*-dien-14-one	H	Ac	H	iBu	OMeBu	H	H	*E. terracina*	43
92	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *R**,13 *S**,15 *R**)-5,7,8,9,15-pentaacetoxy-3*β*-benzoyloxyjatropha-6(17),11 *E*-dien-14-one	H	Bz	Ac	Ac	OAc	Ac	Ac	*E. mongolica*	49
93	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-7,8,9-triacetoxy-3,15-dihydroxy-2,5-bis(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	OMeBu	H	MeBu	Ac	OAc	Ac	H	*E. obtusifolia*	50
94	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-7,8,9-triacetoxy-3,7,8,9,15-pentahydroxy-2-isobutyryloxy-5-(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	OiBu	H	MeBu	Ac	OAc	Ac	H	*E. obtusifolia*	50
95	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-7,8,9-triacetoxy-3,15-dihydroxy-2-nicotinoyloxy-5-(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	ONic	H	MeBu	Ac	OAc	Ac	H	*E. obtusifolia*	50
96	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-8,9-diacetoxy-3,15-dihydroxy-7-isobutyryloxy-2,5-bis(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	OMeBu	H	MeBu	iBu	OAc	Ac	H	*E. obtusifolia*	50
97	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-2,8,9-triacetoxy-3,15-dihydroxy-7-isobutyryloxy-5-(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	OAc	H	MeBu	iBu	OAc	Ac	H	*E. obtusifolia*	50
98	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-7,9-diacetoxy-8-benzoyloxy-5,8,15-trihydroxy-2,3-bis(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	OMeBu	MeBu	H	Ac	OBz	Ac	H	*E. obtusifolia*	50
99	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-8,9-diacetoxy-5,15-dihydroxy-7-isobutyryloxy-2,3-bis(2-methylbutanoyloxy)jatropha-6(17),11-dien-14-one	OMeBu	MeBu	H	iBu	OAc	Ac	H	*E. obtusifolia*	50
100	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-2,3,8,9-tetraacetoxy-15-hydroxy-5,7-diisobutyryloxyjatropha-6(17),11-dien-14-one	OAc	Ac	iBu	iBu	OAc	Ac	H	*E. terracina*	43
101	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-2,3,8,9-tetraacetoxy-5-benzoyloxy-15-hydroxy-7-isobutyryloxyjatropha-6(17),11-dien-14-one	OAc	Ac	Bz	iBu	OAc	Ac	H	*E. terracina*	43
102	(2 *R*,3 *R*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*-2,5,8,9-tetraacetoxy-3-(benzoyloxyacetoxy)-15-hydroxy-7-isobutyryloxyjatropha-6(17),11-dien-14-one	OAc	BzOAc	Ac	iBu	OAc	Ac	H	*E. terracina*	43
									E. dendroides	51
103	euphodendroidin A	OAc	H	iBu	Bz	OAc	Ac	H	*E. dendroides*	51
104	euphodendroidin B	OAc	H	MeBu	Bz	OAc	Ac	H	*E. dendroides*	51
105	euphodendroidin C	OAc	H	Nic	Bz	OAc	Ac	H	*E. dendroides*	51
106	euphodendroidin D	H	H	iBu	Bz	OAc	Ac	H	*E. dendroides*	51
107	euphodendroidin E	H	Ac	iBu	Bz	OAc	Ac	H	*E. dendroides*	51
108	euphodendroidin F	OH	Ac	iBu	Bz	OAc	Ac	H	*E. dendroides*	51
109	euphodendroidin G	OAc	Nic	Ac	iBu	OAc	Ac	H	*E. dendroides*	51
110	euphodendroidin H	H	Bz	Ac	iBu	OAc	Ac	H	*E. dendroides*	51
111	euphodendroidin I	ONic	Ac	iBu	Ac	OAc	Nic	Ac	*E. dendroides*	51
112	altotibetin A	H	Ac	Bz	Ac	OAc	Ac	Ac	*E. mongolica*	49
									E. altotibetic	52
113	altotibetin B	H	Ac	Bz	Bu	OAc	Ac	Ac	*E. altotibetic*	52
114	altotibetin C	OH	Ac	Bz	Ac	OAc	Ac	Ac	*E. altotibetic*	52
115	altotibetin D	OH	Ac	Bz	Bu	OAc	Ac	Ac	*E. altotibetic*	52

Table 16. Jatrophanes-6



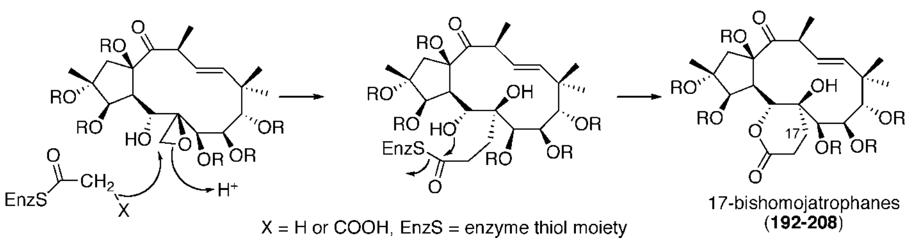
No.	name	R_1	R_2	R_3	R_4	plant	ref
116	esulatin D	OAc	Ac	H	Ac	*E. esula*	53
117	esulatin F	OAc	iBu	OAc	Ac	*E. esula*	54
118	(2 *R**,3 *R**,4 *S**,5 *R**,7 *R**,9 *R**,13 *R**,15 *R**)-2,3,5,7,15-pentaacetoxy-9-nicotinoyloxyjatropha-6(17),11 *E*-dien-14-one	OAc	Ac	H	Nic	*E. peplus*	44
119	3*β*,5α,7*β*,15*β*-tetraacetoxy-9-nicotinoyloxyjatropha-6(17),11*E*-dien-14-one	H	Ac	H	Nic	*E. peplus*	55

Table 17. Jatrophanes-7

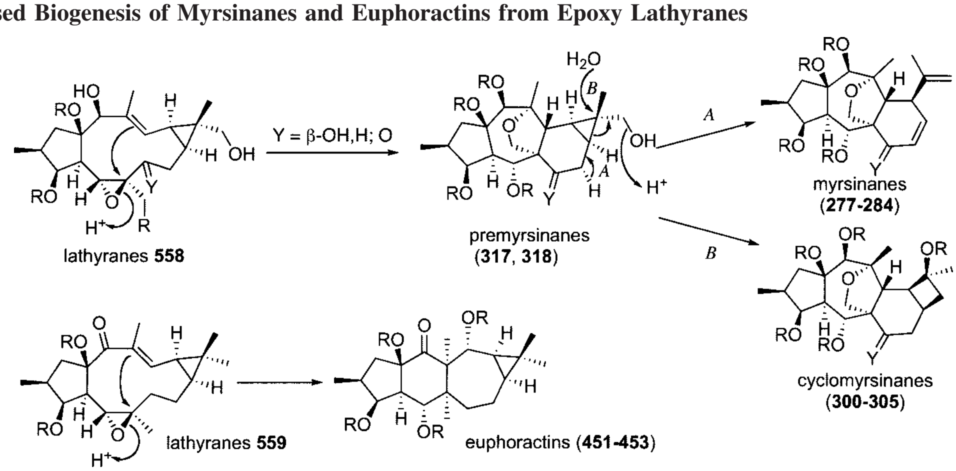


no.	name	R_1	R_2	R_3	R_4	R_5	R_6	plant	ref
120	amygdaloidins A	Ac	Ac	Ang	Ang	Nic	H	*E. amygdaloides*	56
121	amygdaloidins B	Ang	H	Ang	Ac	Nic	H	*E. amygdaloides*	56
122	amygdaloidins C	Hydrp	H	Ang	Ac	Nic	H	*E. amygdaloides*	56
123	amygdaloidins D	Ang	H	Ang	Ac	Ac	H	*E. amygdaloides*	56
124	amygdaloidins E	Ang	H	Hydrp	Ac	Ac	H	*E. amygdaloides*	56
125	amygdaloidins F	Ang	H	Hydrp	Ac	Ac	Ac	*E. amygdaloides*	56
126	amygdaloidins G	Ang	Ac	H	Hydrp	Ac	H	*E. amygdaloides*	56
127	amygdaloidins H	Hydrp	Ac	H	Ang	Ac	H	*E. amygdaloides*	56
128	amygdaloidins I	Ac	Hydrp	H	Ang	Ac	H	*E. amygdaloides*	56
129	amygdaloidins J	Hydrp	Ac	Ang	H	Ac	H	*E. amygdaloides*	56
130	amygdaloidins K	Ac	Hydrp	Ang	H	Ac	H	*E. amygdaloides*	56
131	amygdaloidins L	Ang	Ac	Hydrp	H	Ac	H	*E. amygdaloides*	56

Scheme 4. Proposed Biogenesis of Lactones (192−208) by Incorporation of a C2 Unit (from Acetate or Malonate) into a Jatrophane Precursor



Scheme 5. Proposed Biogenesis of Myrsinanes and Euphoractins from Epoxy Lathyranes



2.3.5. Jatropholanes (Table 44)

Lagaspholones A (**324**) and B (**325**) belong to jatropholanes are a new class of members with a 5,12-cyclojatrophane skeleton.[115]

Scheme 6. Proposed Biogenetic Routes of Lagaspholone A (324)

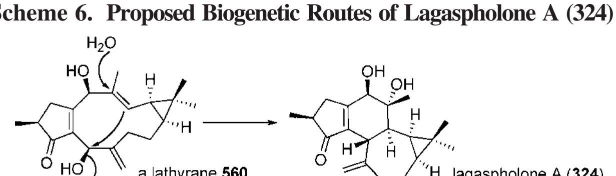
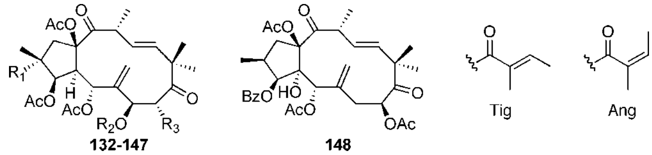
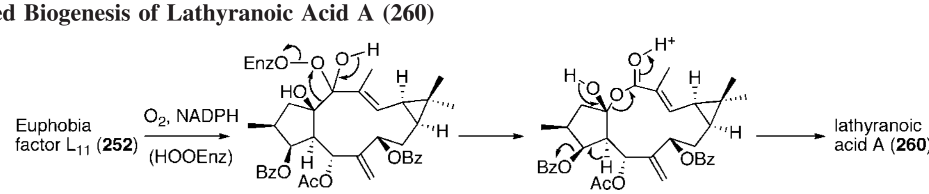


Table 18. Jatrophanes-8



no.	name	R_1	R_2	R_3	plant	ref
132	(2 *R*,3 *R*,4 *S*,5 *R*,7 *S*,8 *R*,13 *R*,15 *R*)-2,3,5,7,15-pentaacetoxy-8-isobutyryloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OiBu	*E. semiperfoliata* *E. paralias*	23 57
133	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,7,15-pentaacetoxy-8-tigloyloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OTig	*E. semiperfoliata*	23
134	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,7,15-pentaacetoxy-8-benzoyloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OBz	*E. semiperfoliata*	23
135	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-3,5,7,8,15-pentaacetoxy-2-nicotinoyloxyjatropha-6(17),11 *E*-diene-9,14-dione	Nic	Ac	OAc	*E. semiperfoliata*	23
136	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,8,15-pentaacetoxy-7-benzoyloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Bz	OAc	*E. semiperfoliata* *E. turczaninowii*	23 58
137	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,8,15-pentaacetoxy-7-isobutyryloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	iBu	OAc	*E. semiperfoliata*	23
138	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-3,5,7,8,15-pentaacetoxy-2-benzoyloxyjatropha-6(17),11 *E*-diene-9,14-dione	OBz	Ac	OAc	*E. semiperfoliata*	23
139	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,7,15-pentaacetoxy-8-hydroxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OH	*E. semiperfoliata*	23
140	(2 *R**,3 *R**,4 *S**,5 *R**,7 *R**,13 *R**,15 *R**)-2,3,5,15-tetraacetoxy-7-isobutyryloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	iBu	H	*E. semiperfoliata*	23
141	esulatin B	OAc	Ac	H	*E. seguieriana* *E. semiperfoliata*	58 23
142	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,7,15-pentaacetoxy-8-isobutyryloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OiBu	*E. paralias*	59
143	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,7,15-pentaacetoxy-8-angeloyloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OAng	*E. paralias*	59
144	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-3,5,7,15-tetraacetoxy-8-isobutyryloxyjatropha-6(17),11 *E*-diene-9,14-dione	H	Ac	OiBu	*E. paralias*	59
145	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,7,15-pentaacetoxy-8-(2-methylbutanoyloxy)jatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OMeBu	*E. paralias*	59
146	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,7,15-pentaacetoxy-8-benzoyloxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OBz	*E. paralias*	59
147	(2 *R**,3 *R**,4 *S**,5 *R**,7 *S**,8 *R**,13 *R**,15 *R**)-2,3,5,7,8,15-hexaacetoxyjatropha-6(17),11 *E*-diene-9,14-dione	OAc	Ac	OAc	*E. paralias* *E. semiperfoliata*	59 23
148	pubescenol: 5α,8β,15β-triacetoxy-3β-benzoyloxy-4α-hydroxy-13βH-jatropha-6(17),11*E*-diene-9,14-dione	–	–	–	*E. pubescens*	26

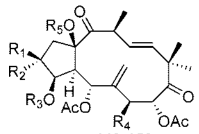
Scheme 7. Proposed Biogenesis of Lathyranoic Acid A (260)



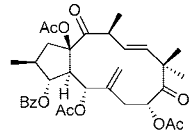
2.3.6. Daphnanes (Table 45)

Resiniferatoxin (**326**) and **327** forms intramolecular orthoester with phenylacetic acid.[116,117,119] Langduin A (**328**), possessing an isopropyl group at C-14 and carbonyl group at C-13, is presumably derived from a tigliane by opening of the cyclopropane ring.[8]

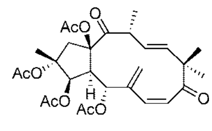
Table 19. Jatrophanes-9



149-153



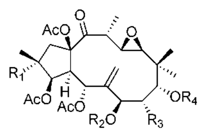
154



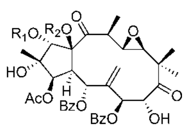
155

no.	name	R_1	R_2	R_3	R_4	R_5	plant	ref
149	3*β*,5α,7*β*,8α,15*β*-pentaacetoxyjatropha-6(17),11*E*-diene-9,14-dione	Me	H	Ac	OAc	Ac	*E. turczaninowii*	48
150	(2 *S*,3 *S*,4 *S*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,15 *R*)-3,5,8,15-tetraacetoxy7-isobutyryloxyjatropha-6(17),11-diene-9,14-dione	Me	H	Ac	OiBu	Ac	*E. terracina*	43
151	(2 *S**,3 *S**,4 *R**,5 *R**,7 *S**,8 *R**,13 *S**,15 *R**)-5,7,8-triacetoxy-3-benzoyloxy-15-hydroxyjatropha-6(17),11 *E*-diene-9,14-dione	Me	H	Bz	OAc	H	*E. mongolica*	49
152	(2 *S**, 3 *S**, 4 *R**, 5 *R**, 8 *R**, 13 *S**, 15 *R**)-5,8,15-triacetoxy-3-benzoyloxyjatropha-6(17),11 *E*-diene-9,14-dione	H	Me	Bz	H	Ac	*E. hyberna*	60
153	3*β*,5α,8α,15*β*-tetraacetoxy-7*β*-benzoyloxyjatropha-6(17),11*E*-diene-9,14-dione	Me	H	Ac	OBz	Ac	*E. turczaninowii*	48
154	euphopubescenol	–	–	–	–	–	*E. pubescens*	61
155	esulatin E	–	–	–	–	–	*E. esula*	53

Table 20. Jatrophanes-10



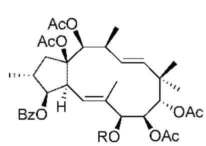
156-161



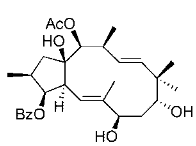
162, 163

no.	name	R_1	R_2	R_3	R_4	plant	ref
156	kansuinin E	H	Ac	OBz	Nic	*E. kansui*	62
157	esulatin A	OAc	iBu	OAc	Ac	*E. esula* *E. salicifolia*	58 63
158	2α,3*β*,5α,9-tetraacetoxy-11,12-epoxy-7*β*,8α-diisobutyryloxyjatroph-6(17)-en-14-one	OAc	iBu	OiBu	Ac	*E. salicifolia*	63
159	2α,3*β*,5α,6*β*,9α-pentaaacetoxy-11,12-epoxy-8α-isobutyryloxyjatroph-6(17)-en-14-one	OAc	Ac	OiBu	Ac	*E. salicifolia*	63
160	kansuinin F	H	Ac	OBz	Bz	*E. kansui*	64
161	kansuinin G	H	Ac	H	Nic	*E. kansui*	64
162	kansuinin C	Ac	H	–	–	*E. kansui*	65
163	kansuinin B	H	Ac	–	–	*E. kansui*	65

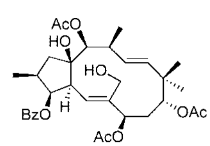
Table 21. Jatrophanes-11



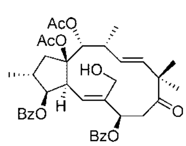
164, 165



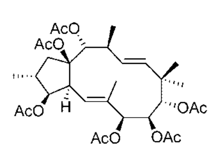
166



167



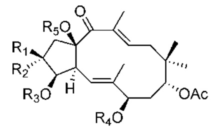
168

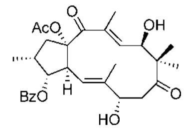


169

no.	name	R	plant	ref
164	(2 *R**,3 *S**,4 *S**,7 *S**,8 *S**,9 *S**,13 *S**,14 *S**,15 *R**)-8,9,14,15-tetraacetoxy-3-benzoyloxyjatropha-5 *E*,11 *E*-dien-7-ol	H	*E. serrulata*	66
165	(2 *R**,3 *S**,4 *S**,7 *S**,8 *S**,9 *S**,13 *S**,14 *S**,15 *R**)-7,8,9,14,15-pentaacetoxy-3-benzoyloxyjatropha-5 *E*,11 *E*-diene	Ac	*E. platyhyllos*	67
166	14*β*-acetoxy-3*β*-benzoyloxyjatropha-5*E*,11 *E*-diene-7*β*,9α,15*β*-triol	–	*E. helioscopia*	68
167	7*β*,9α,14*β*-triacetoxy-3*β*-benzoyloxyjatropha-5 *E*,11 *E*-diene-15*β*,17-diol	–	*E. helioscopia*	68
168	14α,15*β*-diacetoxy-3*β*,7*β*-dibenzoyloxy-17-hydroxy-(2*β*H,13*β*H) jatropha-5 *E*,11 *E*-dien-9-one	–	*E. helioscopia*	68
169	euphopubescene	–	*E. pubescene*	61

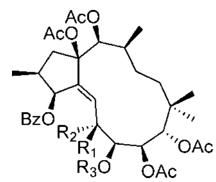
Table 22. Jatrophanes-12


170, 171


172

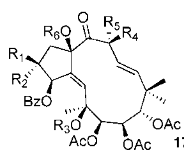
no.	name	R_1	R_2	R_3	R_4	R_5	plant	ref
170	pubescene D	H	Me	Ac	Bz	H	*E. pubescens*	69
171	3*β*,9α,15*β*-triacetoxy-7*β*-butanoyloxyjatropha-5*E*,11 *E*-dien-14-one	Me	H	Ac	Bu	Ac	*E. pubescens*	70
172	euphoheliosnoid D	–	–	–	–	–	*E. helioscopia*	12

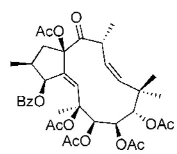
Table 23. Jatrophanes-13

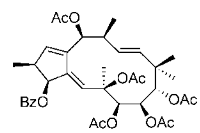


no.	name	R_1	R_2	R_3	plant	ref
173	(2 *S*,3 *S*,6 *S*,7 *R*,8 *R*,9 *S*,13 *S*,14 *S*,15 *R*)-7,8,9,14,15-pentaacetoxy-3-benzoyloxyjatropha-4 *E*,11 *E*-dien-6-ol	OH	Me	Ac	*E. serrulata*	66
174	(2 *S**,3 *S**,6 *S**,7 *R**,8 *R**,9 *S**,13 *S**,14 *S**,15 *R**)-8,9,14,15-tetraacetoxy-3,7-dibenzoyloxyjatropha-4 *E*,11 *E*-dien-6-ol	OH	Me	Bz	*E. serrulata*	66
175	(2 *S**,3* *S*, 6 *R**,7 *R**,8* *R*,9 *S**,13 *S**,14 *S**,15 *R**)-7,8,9,14,15-pentaacetoxy-3-benzoyloxyjatropha-4 *E*,11 *E*-dien-6-ol	Me	OH	Ac	*E. platyphyllos*	67

Table 24. Jatrophanes-14


176-181


182


183

no.	name	R_1	R_2	R_3	R_4	R_5	R_6	plant	ref
176	(2 *R**,3 *R**,6 *S**,7 *R**,8 *R**,9 *S**,13 *S**,15 *R**)-6,7,8,9,15-pentaacetoxy-3-benzoyloxy-2-hydroxyjatropha-4 *E*,11 *E*-dien-14-one	Me	OH	Ac	Me	H	Ac	*E. serrulata*	66
177	(2 *R**,3 *S**,6 *S**,7 *R**,8 *R**,9 *S**,13 *S**,15 *R**)-7,8,9,15-tetraacetoxy-3-benzoyloxy-6-hydroxyjatropha-4 *E*,11 *E*-dien-14-one	H	Me	H	Me	H	Ac	*E. serrulata*	66
								E. platyphyllos	67
178	(2 *R**,3 *S**,6 *S**,7 *R**,8 *R**,9 *S**,13 *S**,15 *R**)-6,7,8,9,15-pentaacetoxy-3-benzoyloxyjatropha-4 *E*,11 *E*-dien-14-one	H	Me	Ac	Me	H	Ac	*E. serrulata*	66
179	(2 *R*,3 *R*,6 *R*,7 *R*,8 *R*,9 *S*,13 *S*,15 *R*)-2,7,8,9-tetraacetoxy-3-benzoyloxy-6,15-dihydroxyjatropha-4 *E*,11 *E*-dien-14-one	Me	OAc	H	Me	H	H	*E. serrulata*	71
180	(2 *R*,3 *R*,6 *S*,7 *R*,8 *R*,9 *S*,13 *S*,15 *R*)-2,6,7,8,9,15-hexaacetoxy-3-benzoyloxyjatropha-4 *E*,11 *E*-dien-14-one	Me	OAc	Ac	Me	H	Ac	*E. serrulata*	71
181	serrulatin B	Me	H	Ac	H	Me	Ac	*E. serrulata*	72
182	(2 *R*,3 *S*,6 *S*,7 *R*,8 *R*,9 *S*,13 *R*,15 *R*)-6,7,8,9,15-pentaacetoxy-3-benzoyloxyjatropha-4 *Z*,11 *E*-dien-14-one	–	–	–	–	–	–	*E. serrulata*	73
183	(2 *S**,3 *S**,6 *S**,7 *R**,8 *R**,9 *S**,13 *S**,14 *S**)-6,7,8,9,14-pentaacetoxy-3-benzoyloxyjatropha-1(15),4 *Z*,11 *E*-triene	–	–	–	–	–	–	*E. serrulata*	73

2.3.7. Tiglianes (Tables 46–48)

12-*O*-Tetradecanoylphorbol 12-acetate (TPA) is a famous tumor promotor. A number of phorbol derivatives were isolated from *Euphorbia* species. Marco et al. presumed that **336** was not a natural product but rather an epimerization product of **331** during the isolation and chromatographic separation.[50] The C-6 of **358** and **359** is an aldehyde group.[21]

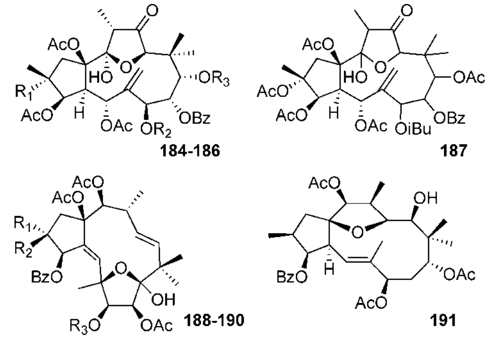
2.3.8. Ingenanes (Tables 49–52)

Ingenane diterpenoids have a very unique structural feature, that is, bicyclo[4.4.1]undecane core adopts a highly strained *inside*–*outside* skeleton. A large number of derivatives have been reported from this genus. Milliamine F isomer (**381**), isolated form *E. leuconeura*, has a unique [(benzamido)benzamido]benzoyl substituent.[128]

2.3.9. Segetanes, Paralianes, Pepluanes, and Euphoractines (Tables 53–58)

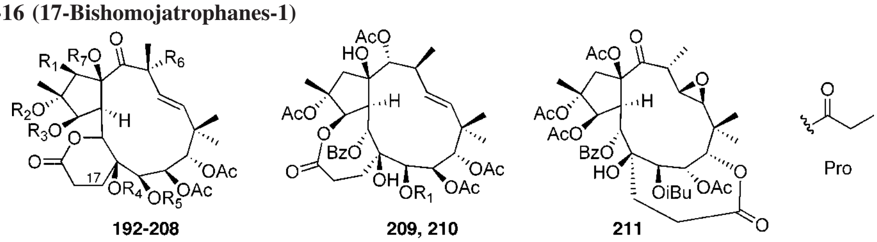
The skeleton of these 5/7/6/5-rings could be formed by transannular ring formation between 8,12- and 13,17-positions of the 12-membered ring of jatrophanes. Presegetanin (**436**) and **435** belong to a new class of carbon skeleton, presumably a biogenetic intermediate from jatrophanes to segetanes.[38,138] Paralianes and pepluanes are

Table 25. Jatrophanes-15 (Jatrophanes with a Hemiacetal or a Tetrahydrofuran Ring)



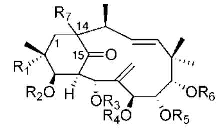
no.	name	R_1	R_2	R_3	plant	ref
184	kansuinin A	H	Ac	Ac	*E. kansui*	65
185	kansuinin H	OH	Ac	Ac	*E. kansui*	64
186	kansuinin D	H	Ac	Nic	*E. kansui*	62
187	esulatin C	–	–	–	*E. esula*	58
188	serrulatin A: (2 *S*,3 *S*,6 *R*,7 *S*,8 *S*,9 *S*,13 *R*,14 *S*,15 *S*)-8,14,15-triacetoxy-3-benzoyloxy-6,9-epoxy-7-tigloyloxyjatropha-4 *Z*,11 *E*-dien-9-ol	H	Me	Tig	*E. serrulata*	72
189	(2 *R*,3 *S*,6 *R*,7 *S*,8 *S*,9 *S*,13 *R*,14 *S*,15 *S*)-8,14,15-triacetoxy-3-benzoyloxy-6,9-epoxy-7-tigloyloxyjatropha-4 *E*,11 *E*-dien-9-ol	Me	H	Tig	*E. serrulata*	71
190	(2 *R*,3 *S*,6 *S*,7 *R*,8 *S*,9 *R*,13 *R*,14 *S*,15 *R*)-8,14,15-triacetoxy-3,7-dibenzoyloxy-6,9-epoxyjatropha-4 *E*,11 *E*-dien-9-ol	Me	H	Bz	*E. platyhyllos*	67
191	7β,9α,14β-triacetoxy-3β-benzoyloxy-12β,15β-epoxyjatroph-5*E*-en-11β-ol	–	–	–	*E. helioscopia*	68

Table 26. Jatrophanes-16 (17-Bishomojatrophanes-1)



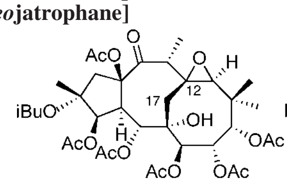
no.	name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	plant	ref
192	terracinolide A	H	Ac	Ac	Bz	iBu	H	Ac	*E. terracina*	73
									E. segetalis	38
193	terracinolide B	H	Ac	Ac	Ac	iBu	H	Ac	*E. terracina*	73
									E. dendroides	74
									E. segetalis	38
194	terracinolide C	H	Ac	H	Ac	iBu	H	Ac	*E. terracina*	75
									E. dendroides	74
									E. segetalis	38
195	terracinolide D	H	Ac	Ac	Bz	Ac	H	Ac	*E. terracina*	75
196	terracinolide E	H	Ac	Ac	Bz	Pr	H	Ac	*E. terracina*	75
									E. segetalis	38
197	terracinolide F	H	Ac	Ac	iBu	iBu	H	Ac	*E. terracina*	75
									E. dendroides	74
198	terracinolide G	H	Ac	Ac	Ac	iBu	H	H	*E. terracina*	75
199	terracinolide H	H	Ac	H	iBu	iBu	H	Ac	*E. segetalis*	38
200	terracinolide J	H	Ac	Ac	iBu	iBu	H	H	*E. dendroides*	74
201	terracinolide K	H	H	Ac	Ac	iBu	H	Ac	*E. dendroide*	74
202	terracinolide L	H	H	Ac	iBu	iBu	H	Ac	*E. dendroides*	74
203	13α-hydroxyterracinolide B	H	Ac	Ac	Ac	iBu	OH	Ac	*E. segetalis*	38
									E. dendroides	74
									E. terracina	28
204	13α-hydroxyterracinolide F	H	Ac	Ac	iBu	iBu	OH	Ac	*E. dendroides*	74
205	13α-hydroxyterracinolide G	H	Ac	Ac	Ac	iBu	OH	H	*E. terracina*	28
									E. dendroides	74
206	15-*O*-deacetyl-13α-hydroxyterracinolide A	H	Ac	Ac	Bz	iBu	OH	H	*E. terracina*	28
207	13α-hydroxyterracinolide I	OAc	Ac	Ac	Ac	iBu	OH	H	*E. segetalis*	38
									E. terracina	28
208	terracinolide I	OAc	Ac	Ac	Ac	iBu	H	H	*E. segetalis*	38
209	isoterracinolide A	iBu	–	–	–	–	–	–	*E. terracina*	28
210	isoterracinolide B	Pr	–	–	–	–	–	–	*E. terracina*	28
211	salicinolide	–	–	–	–	–	–	–	*E. salicifolia*	76

Table 27. Jatrophanes-17 [1(15→14) *Abeo*jatrophanes]

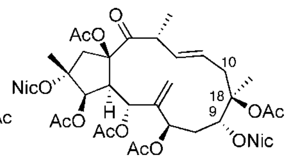


no.	name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	plant	ref
212	(2 *S*,3 *S*,4 *R*,5 *R*,7 *S*,8 *S*,9 *S*,11 *E*,13 *S*,14 *S*)-3,5,7,8,9,14-hexahydroxy-7-isobutyryloxy-5,8-bis(2-methylbutanoyloxy)-1(15→14)*abeo*jatropha-6(17),11-dien-15-one	H	H	MeBu	iBu	MeBu	H	β-OH	*E. terracina*	43
213	abeodendroidin F	OH	Ac	iBu	Bz	Ac	Ac	β-OH	*E. dendroides*	74
214	*epi*-abeodendroidin F	OH	Ac	iBu	Bz	Ac	Ac	α-OH	*E. dendroides*	74

Table 28. Jatrophanes-18 [12,17-Cyclojatrophane and 9(10→18) *Abeo*jatrophane]



215



216

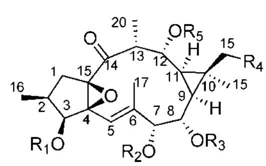
no.	name	plant	ref
215	salicifoline	*E. salicifolia*	76
216	euphosalicin	*E. salicifolia*	63

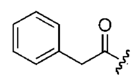
derived from jatrophanes, and euphoractines are from lathyranes (section 3). Compound **445** possesses a rare aromatized D-ring.[38]

2.4. Triterpenoids (Tables 59−65)

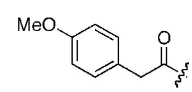
Tetracyclic, pentacyclic triterpenoids, some secotriterpenoids along with several other kinds triterpenoids are isolated from many plants of *Euphorbia* species. Among lanosterol type compounds, antiquol B (**460**) has a rare 19(10→9) *abeo*euphane skeleton.[144] Several oleanes with shifted methyl and desmethyl groups (**477**−**482**) were isolated.[20,26,146,150,153] 27-*Nor*-3β-hydroxycycloartan-25-one (**496**), (22 *E*)-25,26,27-*trinor*-3β-hydroxycycloart-22-en-24-al (**498**) and 25,26,27-*trinor*-3β-hydroxycycloartan-24-al (**499**) are rare *nor*-derivatives reported first in this species.[136] 24-Hydroperoxycycloart-25-en-3β-ol (**500**) is the only C-24 hydroperoxy compound.[136] Peplusol (**508**) is an acyclic triterpene alcohol.[145] Anhydrobisfarnesol (**509**), an anhydro derivative of bisfarnesol, has been isolated from the latex of *E. laterifiora*. Its structure was confirmed by the synthesis using a photochemical isomerization.[158]

Table 29. Lathyranes-1





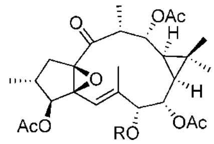
PhAc



A

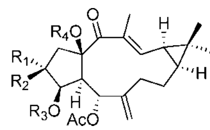
no.	name	R_1	R_2	R_3	R_4	R_5	plant	ref
217	3β,12α-diacetoxy-19-hydroxy-7α,8α-ditigloyloxyingol	Ac	Tigl	Tigl	OH	Ac	*E. acrurensis*	77
218	3β,12α,19-triacetoxy-7α-hydroxy-8α-ditigloyloxyingol	Ac	H	Tigl	OAc	Ac	*E. acrurensis*	77
219	12α,19-diacetoxy-3β,7α-hydroxy-8α-ditigloyloxyingol	H	H	Tigl	OAc	Ac	*E. acrurensis*	77
220	3β,8α,12α-triacetoxy-7α-isovaleryloxyingol	Ac	iVal	Ac	H	Ac	*E. acrurensis*	77
221	3β,8α,12α-triacetoxy-7α-angeloxyingol	Ac	Ang	Ac	H	Ac	*E. acrurensis*	77
222	3β,12α-diacetoxy-7α,8α-ditigloyloxyingol	Ac	Tigl	Tigl	H	Ac	*E. acrurensis*	77
223	3β,8α,12α-triacetoxy-7α-tigloyloxyingol	Ac	Tigl	Ac	H	Ac	*E. acrurensis*	77
224	3β,12α-diacetoxy-8α-methoxy-7α-tigloyloxyingol	Ac	Tigl	Me	H	Ac	*E. acrurensis*	77
225	3β,12α-triacetoxy-7α-hydroxy-8α-tigloyloxyingol	Ac	H	Tigl	H	Ac	*E. acrurensis*	77
							E. lactea	78
226	3β,7α,12α-triacetoxy-8α-isovaleryloxyingol	Ac	Ac	iVal	H	Ac	*E. tirucalli*	79
227	3β,7α,12α-triacetoxy-8α-benzoyloxyingol	Ac	Ac	Bz	H	Ac	*E. nivulia*	80
							E. kamerunica	81
							E. hermentiana	82
228	3β,12α-diacetoxy-7α-angeloyloxy-8α-methoxyingol	Ac	Ang	Me	H	Ac	*E. nivulia*	80
							E. hermentiana	81
229	12α-acetoxy-7α-angeloyloxy-3β-hydroxy-8α-methoxyingol	H	Ang	Me	H	Ac	*E. nivulia*	80
							E. ingens	83
230	3β,12α-diacetoxy-8α-benzoyloxy-7α-hydroxyingol	Ac	H	Bz	H	Ac	*E. nivulia*	80
231	3β,12α-diacetoxy-7α-benzoyloxy-8α-nicotinoyloxyingol	Ac	Bz	Nic	H	Ac	*E. nivulia*	80
232	3β-acetoxy-7α-angeloyloxy-12α-hydroxy-8α-methoxyingol	Ac	Ang	Me	H	H	*E. nivulia*	84
233	3β,12α-diacetoxy-8α-methoxy-7α-hydroxyingol	Ac	H	Me	H	Ac	*E. nivulia*	84
234	3β,12α-diacetoxy-7α-angeloyloxy-8α-hydroxyingol	Ac	Ang	H	H	Ac	*E. nivulia*	84
235	3β,12α,19-triacetoxy-8α-nicotinoyloxy-7α-phenylacetoxyingol	Ac	PhAc	Nic	OAc	Ac	*E. poisonii*	85
236	3β,12α,19-triacetoxy-8α-hydroxy-7α-phenylacetoxyingol	Ac	PhAc	H	OAc	Ac	*E. poisonii*	85
237	3β,19-diacetoxy-8α,12α-dihydroxy-7α-phenylacetoxyingol	Ac	PhAc	H	OAc	H	*E. poisonii*	85
238	7α,8α,12α-triacetoxy-3β-phenylacetoxyingol	PhAc	Ac	Ac	H	Ac	*E. officinarum*	86
239	7α,8α,12α-triacetoxy-3β-(*p*-methoxyphenyl)acetoxyingol	A	Ac	Ac	H	Ac	*E. officinarum*	86
240	7α,12α-diacetoxy-8α-methoxy-3β-phenylacetoxyingol	PhAc	Ac	Me	H	Ac	*E. officinarum*	86

Table 30. Lathyranes-2



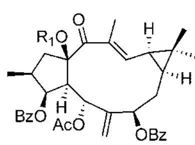
no.	name	R	plant	ref
241	3β,7α,8α,12α-tetraacetoxy-2-*epi*-ingol	Ac	*E. portulacoides*	16
242	3β,8α,12α-triacetoxy-7α-isobutanoyloxy-2-*epi*-ingol	iBu	*E. portulacoides*	16
243	3β,8α,12α-triacetoxy-7α-methylbutanoyloxy-2-*epi*-ingol	MeBu	*E. portulacoides*	16
244	3β,8α,12α-triacetoxy-7α-benzoyloxy-2-*epi*-ingol	Bz	*E. portulacoides*	16

Table 31. Lathyranes-3.

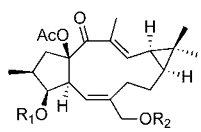


no.	name	R_1	R_2	R_3	R_4	plant	ref
245	(2 *R**,3 *S**,4 *R**,5 *R**,9 *S**,11 *S**,15 *R**)-5α,15β-diacetoxy-3β-benzoyloxylathyra-6(17),12 *E*-dien-14-one	Me	H	Bz	Ac	*E. hyberna*	60
246	(2 *R**,3 *S**,4 *R**,5 *R**,9 *S**,11 *S**,15 *R**)-3,5,15-triacetoxy-lathyra-6(17),12 *E*-dien-14-one	Me	H	Ac	Ac	*E. hyberna*	60
						E. villosa	87
247	Euphorbia factor L_3	H	Me	Bz	Ac	*E. lathyris*	88
248	Euphorbia factor L_8	H	Me	Nic	Ac	*E. lathyris*	88
249	(2 *S**,3 *S**,4 *R**,5 *R**,9 *S**,11 *S**,15 *R**)-5-acetoxy-3-benzoy-loxy-15-hydroxylathyra-6(17),12 *E*-dien-14-one	H	Me	Bz	H	*E. lathyris*	89
250	(2 *S**,3 *S**,4 *R**,5 *R**,9 *S**,11 *S**,15 *R**)-5,15-diacetoxy-3-phenylacetoxylathyra-6(17),12 *E*-dien-14-one	H	Me	PhAc	Ac	*E. pithyusa* subsp. *cupanii*	90

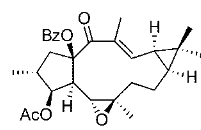
Table 32. Lathyranes-4



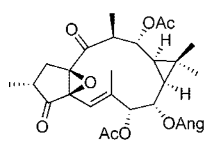
251, 252



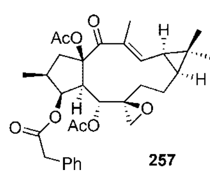
253, 254



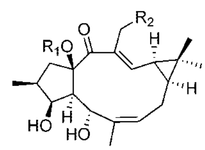
255



256



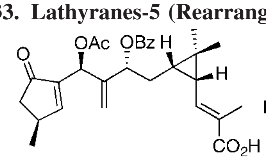
257



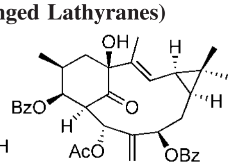
258, 259

no.	name	R_1	R_2	plant	ref
251	Euphorbia factor L $_2$	Ac	–	*E. lathyris*	88
252	Euphorbia factor L_{11}	H	–	*E. lathyris*	91
253	Euphorbia factor L_{10}	$C_5H_{11}CO$	H	*E. lathyris*	92
254	15β,17-diacetoxy-3β-benzoyloxyisolathyrol	Bz	Ac	*E. lathyris*	93
255	(2 *R**,3 *S**,4 *R**,5 *R**,6 *R**,11 *S**,15 *R**)-3-acetoxy-15-benzoyloxy-5,6-epoxylathyr-12 *E*-en-14-one	–	–	*E. villosa*	87
256	(2 *R**,4 *R**,7 *R**,8 *S**,9 *S**,11 *R**,12 *S**,13 *S**,15 *R**)-7,12-diacetoxy-8-angeloyloxy-4,15-epoxylathyr-5 *E*-ene-3,14-dione	–	–	*E. segetalis*	93
257	Euphorbia factors L_1	–	–	*E. lathyris*	88
				E. pithyusa subsp. *cupanii*	90
258	15β-cinnamoyloxy-3β,5α-dihydroxylathyra-6*Z*,12 *E*-dien-14-one	Cinn	H	*E. kansuensis*	94
259	15β-cinnamoyloxy-3β,5α,20-trihydroxylathyra-6*Z*,12 *E*-dien-14-one	Cinn	OH	*E. kansuensis*	94

Table 33. Lathyranes-5 (Rearranged Lathyranes)



260



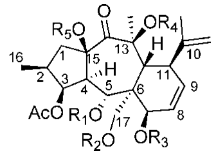
261

no.	name	plant	ref
260	lathyranoic acid A	*E. lathyris*	91
261	lathyranone A	*E. lathyris*	95

2.5. Steroids (Tables 66 and 67)

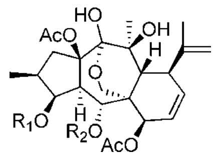
Tanaka et al. isolated several ergostane-type steroids (**510-515**) from *E. chamaesyce*.[149,151] 5α-Stigmastane-3β,6α-diol (**517**) and 5α-stigmastane-3β,5,6β-triol (**519**) were found to be obtained in *E. boetica*.[111] In 2002, Rahman et al. reported the isolation of a new geniculatoside (**519**) from aerial parts of *E. geniculata* Linn.[159] In addition, β-sitosterol and daucosterol are present in many plants of this species, such

Table 34. Myrsinanes-1



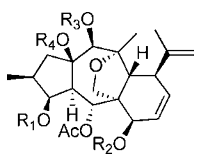
no.	name	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	plant	ref
262	13-deacetylisodecipidone	Bu	H	Ac	H	Ac	*E. decipiens*	96
263	13-deacetylisodecipinone	Bz	H	Ac	H	Ac	*E. decipiens*	96
264	isodecipidone	Bu	H	Ac	Ac	Ac	*E. decipiens*	96
265	17-acetoxy-13-deacetyldecipinone	Bz	Ac	Ac	H	Ac	*E. decipiens*	97
266	13-deacetyldecipinone	Bz	Ac	Ac	H	H	*E. decipiens*	97
267	13-deacetyldecipidone	Bu	Ac	Ac	H	H	*E. decipiens*	97
268	decipinone	Bz	Ac	Ac	Ac	H	*E. decipiens*	98,99
269	decipidone	Bu	Ac	Ac	Ac	H	*E. decipiens*	98
270	isodecipinone	Bz	H	Ac	Ac	Ac	*E. decipiens*	98
271	17-acetoxy-13-deacetylisodecipidone	Bu	Ac	Ac	H	Ac	*E. decipiens*	100

Table 35. Myrsinanes-2



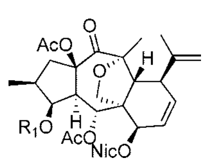
no.	name	R$_1$	R$_2$	plant	ref
272	3β,7β,15β-tri-*O*-acetyl-5α-*O*-nicotinoyl-13β,14β-dihydroxy-14-desoxo-14α,6α-epoxymethanomyrsinol	Ac	Nic	*E. decipiens*	101
273	decipinol ester A	Bu	Nic	*E. decipiens*	96
274	decipinone B	Ac	Bz	*E. decipiens*	102
275	decipinone C	Ac	Bu	*E. decipiens*	102
276	3β,7β,15β-tri-*O*-acetyl-5α-*O*-benzoyl-13β,14β-dihydroxy-14-desoxo-14α,6α-epoxymethanomyrsinol	Bu	Bz	*E. decipiens*	101

Table 36. Myrsinanes-3



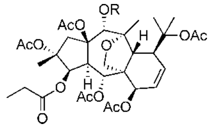
no.	name	R$_1$	R$_2$	R$_3$	R$_4$	plant	ref
277	euphorprolitherin C: 5α,15β-di-*O*-acetyl-7β,14β-di-*O*-benzoyl-14-desoxo-3β-*O*-propanoylmyrsinol	Pr	Bz	Bz	Ac	*E. prolifera*	103
278	5α,15β-di-*O*-acetyl-7β,14β-di-*O*-nicotinoyl-14-desoxo-3β-*O*-propanoylmyrsinol	Pr	Nic	Nic	Ac	*E. seguieriana*	19
279	3β,5α,15β-tri-*O*-acetyl-7β,14β-di-*O*-nicotinoyl-14-desoxomyrsinol	Ac	Nic	Nic	Ac	*E. seguieriana*	19
280	3β,5α,15β-tri-*O*-acetyl-7β-*O*-benzoyl-14β-*O*-nicotinoyl-14-desoxomyrsinol	Ac	Bz	Nic	Ac	*E. seguieriana*	19
281	5α,15βdi-*O*-acetyl-7β-*O*-benzoyl-14β-*O*-nicotinoyl-14-desoxo-3β-*O*-propanoylmyrsinol	Pr	Bz	Nic	Ac	*E. seguieriana*	19
282	5α,14β,15β-tri-*O*-acetyl-7β -*O*-benzoyl-14-desoxo-3β-*O*-propanoylmyrsinol	Pr	Bz	Ac	Ac	*E. seguieriana*	19
283	5α,14β,15β-tri-*O*-acetyl-7β-*O*-nicotinoyl-14-desoxo-3β-*O*-propanoylmyrsinol	Pr	Nic	Ac	Ac	*E. seguieriana*	19
284	5α14β-di-*O*-acetyl-15β-hydroxy-7β-*O*-nicotinoyl-14-desoxo-3β-*O*-propanoylmyrsinol	Pr	Nic	Ac	H	*E. seguieriana*	19

Table 37. Myrsinanes-4



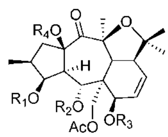
no.	name	R$_1$	R$_2$	plant	ref
285	15β-*O*-acetyl-3β-*O*-butanoyl-7β-*O*-nicotinoyl-5α-*O*-propanoylmyrsinol	Bu	Pr	*E. myrsinites*	104
286	15β-*O*-acetyl-3β,5α-di-*O*-butanoyl-7β-*O*-nicotinoylmyrsinol	Pr	Pr	*E. myrsinites*	104
287	15β-*O*-acetyl-7β-*O*-nicotinoyl-3β,5α-di-*O*-propanoylmyrsinol	Bu	Bu	*E. myrsinites*	104
288	15β-*O*-acetyl-5α-*O*-butanoyl-7β-*O*-nicotinoyl-3β-*O*-propanoylmyrsinol	Pr	Bu	*E. myrsinites*	104

Table 38. Myrsinanes-5

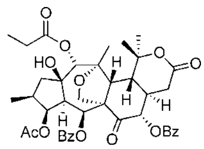


no.	name	R	plant	ref
289	euphorprolitherin A	Bz	*E. prolifera*	103
290	euphorprolitherin B	MeBu	*E. prolifera*	103

Table 39. Myrsinanes-6



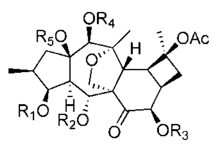
291-298



299

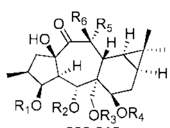
no.	name	R1	R2	R3	R4	plant	ref
291	3*β*-*O*-benzoyl-5α,7*β*,17-tri-*O*-acetyl-15*β*-hydroxycheiradone	Bz	Ac	Ac	H	*E. decipiens*	101
292	3*β*,5α,17-tri-*O*-acetyl-7*β*-*O*-benzoyl-15*β*-hydroxycheiradone	Ac	Ac	Bz	H	*E. decipiens*	105
293	3*β*,5α,15*β*,17-tetra-*O*-acetyl-7*β*-*O*-benzoylcheiradone	Ac	Ac	Bz	Ac	*E. decipiens*	105
294	3*β*,5α,15*β*,17-tetra-*O*-acetyl-7*β*-*O*-nicotinoylcheiradone	Ac	Ac	Nic	Ac	*E. decipiens*	105
295	15*β*-*O*-acetylcheiradone	Ac	Bz	Ac	Ac	*E. decipiens*	96
296	cheiradone	Ac	Bz	Ac	H	*E. cheiradenia*	106
297	cheiradone A	Ac	Bz	H	H	*E. cheiradenia*	106
298	cheiradone B	H	Bz	Ac	H	*E. cheiradenia*	106
299	myrsinol analog with C_9-C_{10} lactone ring	–	–	–	–	*E. prolifera*	107

Table 40. Cyclomyrsinanes

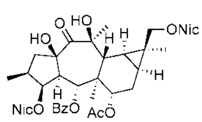


no.	name	R1	R2	R3	R4	R5	plant	ref
300	3*β*,5α,10*β*,14*β*,15*β*-penta-*O*-acetyl-8*β*-*O*-(2-methylbutanoyl)cyclomyrsinol	Ac	Ac	MeBu	Ac	Ac	*E. teheranica*	108
301	5α,10*β*,14*β*,15*β*-tetra-*O*-acetyl-8*β*-*O*-(2-methylbutanoyl)-3*β*-*O*-nicotinoylcyclomyrsinol	Nic	Ac	MeBu	Ac	Ac	*E. teheranica*	108
302	3*β*,10*β*,15*β*-tri-*O*-acetyl-8*β*-*O*-isobutyryl-5α,14*β*-*O*-dinicotinoylcyclomyrsinol	Ac	Nic	iBu	Nic	Ac	*E. seguieriana*	109
303	5α,10*β*,15*β*-tri-*O*-acetyl-8*β*,14*β*-*O*-dinicotinoyl-3*β*-*O*-propanoylcyclomyrsinol	Pr	Ac	Nic	Nic	Ac	*E. seguieriana*	19
304	euphorprolitherin D: 5α,10*β*,14*β*-tri-*O*-acetyl-8*β*-*O*-benzoyl-3*β*-*O*-propanoylcyclomyrsinol	Pr	Ac	Bz	Ac	H	*E. prolifera*	103
305	*s*Pr5	Pr	Ac	Bz	Ac	Ac	*E. prolifera*	110

Table 41. Premyrsinanes-1



306-315



316

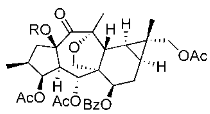
no.	name	R1	R2	R3	R4	R5	R6	plant	ref
306	eufoboetol	H	H	H	H	OH	Me	*E. boetica*	111
307	kandovanol ester A	Ac	Bz	Ac	Ac	Me	OH	*E. decipiens*	96
308	kandovanol ester B	Ac	Bu	Ac	Ac	Me	OH	*E. decipiens*	96
309	3*β*,7*β*,13*β*,17-tetraacetoxy-5α-isobutyryloxypremyrsinol	Ac	iBu	Ac	Ac	Me	OAc	*E. pithyusa* subsp. *cupanii*	90
310	7*β*,13*β*,17-triacetoxy-5α-isobutyryloxy-3*β*-propanoyloxypremyrsinol	Pr	iBu	Ac	Ac	Me	OAc	*E. pithyusa* subsp. *cupanii*	90
311	7*β*,13-diacetoxy-l5α-isobutyryloxy-17-nicotinoyloxy-3*β*-propanoyloxypremyrsinol	Pr	iBu	Nic	Ac	Me	OAc	*E. pithyusa* subsp. *cupanii*	90
312	7*β*,13*β*-diacetoxy-17-isobutyryloxy-5-(2-methylbutanoyloxy)-3*β*-propanoyloxypremyrsinol	Pr	MeBu	iBu	Ac	Me	OAc	*E. pithyusa* subsp. *cupanii*	90
313	7*β*,13*β*-diacetoxy-5α,17-diisobutyryloxy-3*β*-propanoyloxypremyrsinol	Pr	iBu	iBu	Ac	Me	OAc	*E. pithyusa* subsp. *cupanii*	90
314	7*β*,13*β*-diacetoxy-5α-isobutyryloxy-3*β*,17-dipropanoyloxypremyrsinol	Pr	iBu	Pr	Ac	Me	OAc	*E. pithyusa* subsp. *cupanii*	90
315	7*β*,13*β*,17-triacetoxy-5α-benzoyloxy-3*β*-propanoyloxypremyrsinol	Pr	Bz	Ac	Ac	Me	OAc	*E. pithyusa* subsp. *cupanii*	90
316	7α-*O*-acetyl-5*β*-*O*-benzoyl-13*β*-hydroxy-3*β*,18-dinicotinoyloxypremyrsinol	–	–	–	–	–	–	*E. seguieriana*	109

as *E. boetica*, *E. segetalis*, *E. altotibetic*, *E. aleppica*, *E. quinquecostata*, and *E. latifolia*.[30,52,111,114,147,150]

2.6. Cerebrosides and Glycerols (Tables 68 and 69)

A complex mixture of four glucocerebrosides, **522** (n = 21), **523** (n = 1, 3), and **524**, was isolated from *E. peplis*.[163]

Table 42. Premyrsinanes-2



no.	name	R	plant	ref
317	karajinone A	Ac	*E. decipiens*	112
318	karajinone B	H	*E. decipiens*	112

These were the first examples of glycosphingolipids from the *Euphorbia* genus. Other cerebrosides (**522**−**526**) and a sphingosine (**527**) have been isolated from several species.

Cateni et al. isolated three new glycolipids (**528**, **530**, and **531**) with anti-inflammatory activity from *E. cyparissias*.[167]

2.7. Phenolics (Tables 70 and 71)

Several acetophenones and its glycoside were isolated from *E. portulacoides*, *E. quinquecostata*, *E. quinquecostata*, *E. fischeriana*, and *E. ebracteolata*.[13,16,30,168] Unusual phenol dimers (**541** and **542**) were reported from *E. ebracteolata*.[168]

2.8. Flavonoids (Table 72)

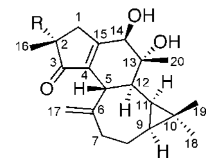
In 2004, a new flavonol glycoside, quercetin 3-*O*-6′-(3-hydroxyl-3-methylglutaryl)-*β*-D-glucopyranoside (**543**), and four known flavonoids, kaempferol 3-*O*-2″-galloyl-*β*-D-glucopyranoside, kaempferol 3-*O*-rutinoside, quercetin 3-*O*-*β*-D-glucopyranoside, and rutin, were isolated from the aerial parts of *E. ebracteolata.*[169] Nishimura et al. reported the isolation of one new flavonoid galactoside, quercetin 3-*O*-(2″,3″-digalloyl)-*β*-D-galactopyranoside (**544**), from *E. lunulata*, along with four known ones, quercetin 3-*O*-(2″-galloyl)-*β*-D-galactopyranoside (**545**), hyperin, and quercetin.[170] Recently, Zhang et al. reported six known flavonoids such as licochalcone A, 4,2′,4′-trihydroxychalcone, echinatia, licochalcone B, glabrone, and 5,7,4′-trihydroxyflavanone from *E. helioscopia.*[12] These compounds were isolated from the species for the first time. In addition, the common flavonoids such as kaempferol, kaempferol 3-*O*-L-rhaside, kaempferol 3-*O*-*β*-D-glucopyranoside, quercetin, quercetin 3-*O*-*β*-D-glucopyranoside, and astragalin have been isolated from many plants of this species such as *E. latifolia*, *E. altotibetic*, and *E. aleppica*.[52,113,114,147]

2.9. Miscellaneous Compounds (Table 73)

Lee et al. isolated a new ellagitannin, jolkinin (**546**), from the fresh whole plant of *E. jolkinii* in 2004.[171] It has a unique hexacyclic structure attached to the 2,4-positions of 1-*O*-galloyl-3,6-(*R*)-hexahydroxydiphenoyl-*β*-D-glucopyranose. 3,3′,4′-Tri-*O*-methyl-4-*O*-[α-L-rhamnopyranosyl-(1″→6″)-*β*-D-glucopyranosyl]ellagic acid has been isolated from *E. quinquecostata.*[30] In 2002, Su et al. isolated a new dihydrobenzo[*b*]furan neolignan, (−)-*trans*-9-acetyl-4,9′-di-*O*-methyl-3′-de-*O*-methyldehydrodiconiferyl alcohol (**547**), from the stem wood of *E. quinquecostata* along with 3,4-dimethoxycinnamaldehyde.[36]

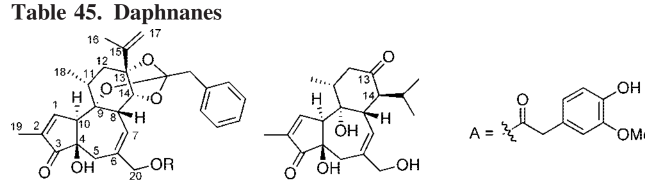
Coumarins in *Euphorbia* genus are not very rich. The main compounds are scopoletin (**548**),[52] 7,7′-dihydroxy-6,8′-bicoumarin (bicoumol, **549**),[36] 6,7,8-trimethoxycoumarin (**550**),[30] and 6-hydroxy-7-methoxycoumarin (isoscopoletin, **551**).[36] Two alkaloids, uracil and uridine, were isolated from *E. altotibetic* in 2003.[52] In 1999, Che et al. reported the isolation of physcion from *E. fischeriana*.[13] Gallic acid, 3,3′-di-*O*-methylellagic acid, and 3,4,3′-tri-*O*-methylellagic acid 4′-*O*-*β*-D-glucopyranoside were isolated from *E. fischeriana*, *E. sessiliflora*, and *E. lunulata*.[13,15,75] Octacosyl ferulate (**552** and **553**),[172] 1-glycerin hexadecanoate, 1-octacosanol, 9- *cis*-tricosene, 4-hydroxybenzoic acid, and its methyl ether were found to exist in *E. fischeriana, E. humifusa*, *E. latifolia*, and *E. aleppica*.[84,113,145,147,148]

Table 44. Jatropholanes



no.	name	R	plant	ref
324	lagaspholone A	H	*E. lagascae*	115
325	lagaspholone B	OH	*E. lagascae*	115

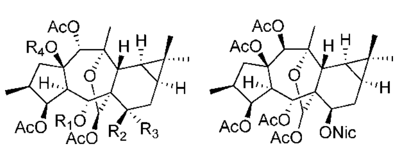
Table 45. Daphnanes



326, **327** **328**

no.	name	R	plant	ref
326	20-(4-hydroxy-3-methoxyphenylacetoxy)-9,13,14-(orthophenylacetoxy)resiniferol (resiniferatoxin)	A	*E. poisonii*	116,117
			E. resinifera	118,119
327	20-hydroxy-9,13,14-(orthophenylacetoxy)resiniferol	H	*E. poisonii*	116
328	langduin A	−	*E. fischeriana*	8

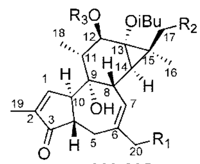
Table 43. Premyrsinanes-3



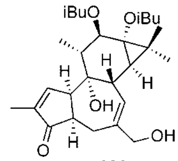
319-322 **323**

no.	name	R_1	R_2	R_3	R_4	plant	ref
319	aleppicatine A	Tigl	H	OAc	Ac	*E. aleppica*	113
320	aleppicatine B	Tigl	H	OAc	Tigl	*E. aleppica*	113
321	euphoreppine A	Ac	OTigl	H	Ac	*E. aleppica*	114
322	euphoreppine B	Ac	OTigl	H	Tigl	*E. aleppica*	114
323	3*β*,5α,14*β*,15*β*,17-penta-*O*-acetyl-7-*O*-nicotinoyleuphoppin	−	−	−	−	*E. decipiens*	96

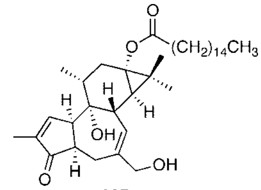
Table 46. Tiglianes-1



329-335



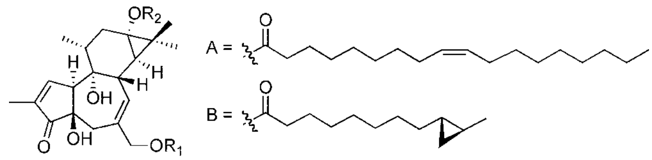
336



337

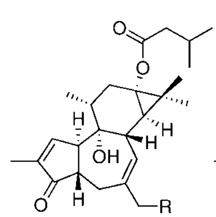
no.	name	R1	R2	R3	plant	ref
329	13α-isobutyryloxy-4-deoxy-12β-tigloyloxyphorbol	OH	H	Tigl	*E. semiperfoliata*	23
330	12β,13α-diisobutyryloxy-4,20-dideoxyphorbol	H	H	iBu	*E. obtusifolia*	50
331	12β,13α-diisobutyryloxy-4-deoxyphorbol	OH	H	iBu	*E. obtusifolia*	50
332	17-acetoxy-12,13α-diisobutyryloxy-4-deoxyphorbol	OH	OAc	iBu	*E. obtusifolia*	50
333	17-acetoxy-12β,13α-diisobutyryloxy-4,20-dideoxyphorbol	H	OAc	iBu	*E. obtusifolia*	50
334	20-acetoxy-12β,13α-diisobutyryloxy-4-deoxyphorbol	OAc	H	iBu	*E. obtusifolia*	50
335	12β-benzoyloxy-13α-isobutyryloxy-4-deoxyphorbol	OH	H	Bz	*E. semiperfoliata*	23
336	12β,13α-diisobutyryloxy-4-deoxy-4-*epi*-phorbol (4-*epi*-**331**)	–	–	–	*E. obtusifolia*	50
337	13α-hexadecanoyl-4,12-dideoxy-4-*epi*-phorbol	–	–	–	*E. guyoniana*	120

Table 47. Tiglianes-2

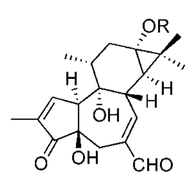


no.	name	R1	R2	plant	ref
338	20-acetoxy-13-isobutyryloxy-12-deoxyphorbol	Ac	iBu	*E. resinifera*	11
339	13-hexadecanoyloxy-12-deoxyphorbol	H	$CO(CH_2)_{14}CH_3$	*E. fischeriana*	8
340	prostratin: 13-acetoxy-12-deoxyphorbol	H	Ac	*E. fischeriana*	8
				E. cornigera	121
341	20-acetoxy-13-(9*Z*-octadecanoyloxy)-12-deoxyphorbol	Ac	A	*E. fischeriana*	21
342	20-acetoxy13-angeloyloxy-12-deoxyphorbol	Ac	Ang	*E. poisonii*	122
				E. resinifera	11
343	20-acetoxy-12-deoxy13-phenylacetoxyphorbol	Ac	PhAc	*E. poisonii*	116
344	20-hydroxy-13-(*E*-9,10-methanoundecanoyloxy)-12-deoxyphorbol	H	B	*E. poisonii*	123
345	13-angeloyloxy-20-hydroxy-12-deoxyphorbol	H	Ang	*E. poisonii*	122
346	13-acetoxy-20-benzoyloxy-12-deoxyphorbol	Ac	Bz	*E. cornigera*	124
347	13-acetoxy-20-*p*-methoxybenzoyloxy-12-deoxyphorbol	Ac	*p*-$MeOC_6H_4CO$	*E. cornigera*	124
348	20-angeloyloxy-13-decanoyloxy-12-deoxyphorbol	$CO(CH_2)_8CH_3$	Ang	*E. cornigera*	124
349	13-decanoyloxy-20-tigloyloxy-12-deoxyphorbol	$CO(CH_2)_8CH_3$	Tigl	*E. cornigera*	124
350	13-acetoxy-20-decanoyloxy-12-deoxyphorbol	Ac	$CO(CH_2)_8CH_3$	*E. cornigera*	124
351	13-butanoyloxy-20-decanoyloxy-12-deoxyphorbol	Bu	$CO(CH_2)_8CH_3$	*E. cornigera*	124
352	20-decanoyloxy-13-hexanoyloxy-12-deoxyphorbol	$CO(CH_2)_4CH_3$	$CO(CH_2)_8CH_3$	*E. cornigera*	124
353	20-decanoyloxy-13-octanoyloxy-12-deoxyphorbol	$CO(CH_2)_6CH_3$	$CO(CH_2)_8CH_3$	*E. cornigera*	124
354	20-decanoyloxy-13-dodecanoyloxy-12-deoxyphorbol	$CO(CH_2)_{10}CH_3$	$CO(CH_2)_8CH_3$	*E. cornigera*	124

Table 48. Tiglianes-3



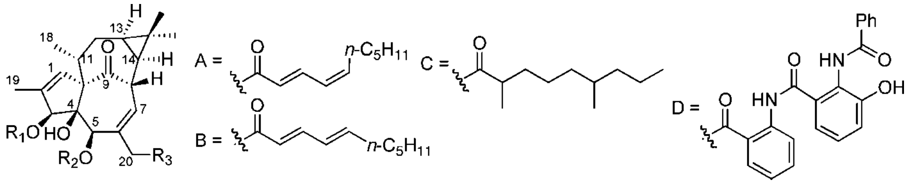
355-357



358, 359

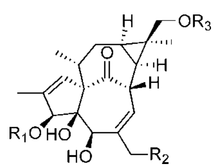
no.	name	R	plant	ref
355	13-(2,3-dimethylbutanoyloxy)-4,12,20-trideoxyphorbol	H	*E. pithyusa* subsp. *cupanii*	90
356	13-(2,3-dimethylbutanoyloxy)-4,12-dideoxyphorbol	OH	*E. pithyusa* subsp. *cupanii*	90
357	20-acetoxy-13-(2,3-dimethylbutanoyloxy)-4,12-dideoxyphorbol	OAc	*E. pithyusa* subsp. *cupanii*	90
358	13-acetoxy-12-deoxyphorbaldehyde	Ac	*E. fischeriana*	21
359	13-hexadecacetoxy-12-deoxyphorbaldehyde	$CO(CH_2)_{14}CH_3$	*E. fischeriana*	21

Table 49. Ingenanes-1



no.	name	R_1	R_2	R_3	plant	ref
360	20-*O*-(2′ *E*,4′ *E*-decadienoyl)ingenol	H	H	OB	*E. kansui*	65
361	20-*O*-(2′ *E*,4′ *Z*-decadienoyl)ingenol	H	H	OA	*E. kansui*	65
362	3*β*-*O*-(2′ *E*,4′ *Z*-decadienoyl)ingenol	A	H	OH	*E. kansui*	65
363	3*β*-*O*-(2′ *E*,4′ *E*-decadienoyl)ingenol	B	H	OH	*E. kansui*	65
364	5*β*-*O*-acetyl-3*β* -*O*-(2′ *E*,4′ *Z*-decadienoyl)ingenol	A	Ac	OH	*E. kansui*	65
365	20-*O*-acetyl-3*β* -*O*-(2′ *E*,4′ *Z*-decadienoyl)ingenol	A	H	OAc	*E. kansui*	65
366	20-*O*-acetyl-3*β* -*O*-(2′ *E*,4′ *E*-decadienoyl)ingenol	B	H	OAc	*E. kansui*	65
367	20-*O*-decanoylingenol	H	H	$OCO(CH_2)_8CH_3$	*E. kansui*	65
368	5*β*-*O*-(2′ *E*,4′ *E*-decadienoyl)ingenol	H	B	OH	*E. kansui*	65
369	20-*O*-myristoylingenol	H	H	$OCO (CH_2)_{12}CH_3$	*E. wallichii*	125
370	3*β*-*O*-myristoylingenol	$CO(CH_2)_{12}CH_3$	H	OH	*E. wallichii*	125
371	3*β*-*O*-angeloylingenol	Ang	H	OH	*E. peplus*	44
372	20-*O*-acetyl-3*β*-*O*-angeloylingenol	Ang	H	OAc	*E. peplus*	44
373	5*β*,20-di-*O*-acetyl-3*β*-*O*-angeloylingenol	Ang	Ac	OAc	*E. acrurensis*	77
					E. canariensis	7
374	3*β*-*O*-angeloyl-20-deoxyingenol	Ang	H	H	*E. paralias*	59
375	kansuiphorin C	Ac	Bz	H	*E. kansui*	126
376	Euphorbia factor L_5: 20-*O*-hexadecanoylingenol	H	H	$OCOC_{15}H_{31}$	*E. quinquecostata*	118
					E. lathyris	127
377	ingenol	H	H	OH	*E. lathyris*	88
378	Euphorbia factor L_4	$COC_{15}H_{31}$	H	OH	*E. lathyris*	88
379	Euphorbia factor L_6	$COC_{14}H_{17}$	H	OH	*E. lathyris*	88
380	ingenol 3*β*-(2,6-dimethylnonanoate)	C	H	OH	*E. resinifera*	11
381	milliamine F isomer	D	H	OPr	*E. leuconeura*	128
382	3*β*-*O*-(2′ *E*,4′ *Z*-decadienoyl)-20-deoxyingenol	A	H	H	*E. kansui*	62
383	3*β*-*O*-(2′ *E*,4′ *E*-decadienoyl)-20-deoxyingenol	B	H	H	*E. kansui*	62
384	20-*O*-acetylingenol	H	H	OAc	*E. segetalis*	38
					E. kansui	129
385	20-deoxyingenol	H	H	H	*E. segetalis*	38
					E. kansui	129

Table 50. Ingenanes-2



no.	name	R_1	R_2	R_3	plant	ref
386	20-acetoxy-3*β*-*O*-angeloyl-17-angeloyloxyingenol	Ang	OAc	Ang	*E. segetalis*	38
387	17-acetoxy-3*β*-*O*-angeloyl-20-deoxyingenol	Ang	H	Ac	*E. acrurensis*	77
388	3*β*-*O*-angeloyl-17-angeloyloxy-20-deoxyingenol	Ang	H	Ang	*E. paralias*	59
					E. segetalis	38
389	3*β*-*O*-benzoyl-17-benzoyloxy-20-deoxyingenol	Bz	H	Bz	*E. portulacoides*	16
390	20-*O*-hexadecanoyl-17-hydroxyingenol	H	$OCO(CH_2)_{14}CH_3$	H	*E. quinquecostata*	30
391	17-(2 *Z*,4 *E*,6 *Z*-2,4,6-tridecanoyloxy)ingenol	H	OH	2,4,6-decatrienoyl	*E. cauducifolia*	130
392	3*β*-*O*-angeloyl-17-(2 *Z*,4 *E*,6 *Z*-tridecanoyloxy)ingenol	Ang	OH	2,4,6-decatrienoyl	*E. cauducifolia*	130
393	3*β*-*O*-acetyl-20-*O*-angeloyl-17-hydroxyingenol	Ac	OAng	H	*E. cauducifolia*	130
394	17-acetoxy-3*β*-*O*-angeloylingenol	Ang	OH	Ac	*E. cauducifolia*	130
395	20-acetoxy-3*β*-*O*-angeloyl-17-hydroxyingenol	Ang	OAc	H	*E. cauducifolia*	130
					E. hermetiana	131
396	3*β*-*O*-angeloyl-17-benzoyloxyingenol	Ang	OH	Bz	*E. cauducifolia*	130
					E. canariensis	132
397	20-acetoxy-3*β*-*O*-angeloyl-17-benzoyloxyingenol	Ang	OAc	Bz	*E. cauducifolia*	130
					E. canariensis	132
398	3*β*-*O*-angeloyl-17-benzoyloxy-20-deoxyingenol	Ang	H	Bz	*E. esula*	133

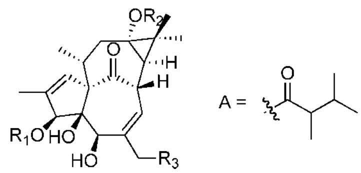
3. Hypothetical Biogenetic Route of the Rearranged Diterpenoids

Most polycyclic and macrocyclic diterpenoids are biosynthesized from geranylgeranyl diphosphate (Scheme 1).[22]

3.1. Biosynthesis from Jatrophanes

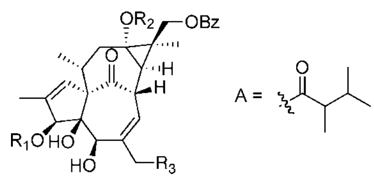
Bicyclic jatrophanes are converted to tetracyclic paralianes and pepluanes as shown in Scheme 2.[44,139] Successive transannular reaction of a jatrophane **554** would

Table 51. Ingenanes-3



no.	name	R$_1$	R$_2$	R$_3$	plant	ref
399	20-*O*-acetyl-l3*β*-*O*-(2,3-dimethylbutanoyl)-13α-*O*-dodecanoylingenol	A	$CO(CH_2)_{10}CH_3$	OAc	*E. kansui*	62
400	3*β*-*O*-(2,3-dimethylbutanoyl)-13α-*O*-dodecanoyl-20-deoxyingenol	A	$CO(CH_2)_{10}CH_3$	H	*E. kansui*	62
401	20-*O*-(2,3-dimethylbutanoyl)-13α-*O*-dodecanoylingenol	H	$CO(CH_2)_{10}CH_3$	OA	*E. kansui*	62
					E. cyparissias	134
402	3*β*-*O*-(2,3-dimethylbutanoyl)-13α-*O*-dodecanoylingenol	A	$CO(CH_2)_{10}CH_3$	OH	*E. kansui*	62
					E. cyparissias	49
403	3*β*-*O*-benzoyl-13α-*O*-dodecanoylingenol	Bz	$CO(CH_2)_{10}CH_3$	OH	*E. kansui*	135
404	20-*O*-benzoyl-13α-*O*-dodecanoylingenol	H	$CO(CH_2)_{10}CH_3$	OBz	*E. kansui*	135
405	3*β*-*O*-(2,3-dimethylbutanoyl)-13α-*O*-octanoylingenol	A	$CO(CH_2)_6CH_3$	OH	*E. esula*	133
406	3*β*-*O*-benzoyl-13α-*O*-octanoylingenol	Bz	$CO(CH_2)_6CH_3$	OH	*E. esula*	133

Table 52. Ingenanes-4



no.	name	R$_1$	R$_2$	R$_3$	plant	ref
407	13α-acetoxy-3*β*-*O*-benzoyl-17-benzoyloxyingenol	Bz	Ac	H	*E. segetalis*	38
408	13α-acetoxy-3*β*-*O*-angeloyl-17-benzoyloxyingenol	Ang	Ac	H	*E. segetalis*	38
409	17-benzoyloxy-3*β*,13α-bis-*O*-(2,3-dimethylbutanoyloxy)ingenol	A	A	H	*E. esula*	133
410	17-benzoyloxy-3*β*,13α-bis-*O*-(2,3-dimethylbutanoyloxy)-20-hydroxyingenol	A	A	OH	*E. esula*	133
411	17-benzoyloxy-13α,20-bis-*O*-(2,3-dimethylbutanoyloxy)-3*β*-hydroxyingenol	H	A	OA	*E. esula*	133
412	17-benzoyloxy-17,20-dihydroxy-13α-octanoyloxyingenol	H	$CO(CH_2)_6CH_3$	OH	*E. esula*	133
413	3*β*,17-dibenzoyloxy-20-hydroxy-13α-octanoyloxyingenol	Bz	$CO(CH_2)_6CH_3$	OH	*E. esula*	133
414	17,20-dibenzoyloxy-3*β*-hydroxy-13α-octanoyloxyingenol	H	$CO(CH_2)_6CH_3$	OBz	*E. esula*	133
415	3*β*-*O*-benzoyl-17-benzoyloxy-13α-octanoyloxyingenol	Bz	$CO(CH_2)_6CH_3$	H	*E. esula*	133
416	17-benzoyloxy-3*β*-*O*-(2,3-dimethylbutanoyloxy)-13α-octanoyloxy-20-hydroxyingenol	A	$CO(CH_2)_6CH_3$	OH	*E. esula*	133
417	17-benzoyloxy-20-(2,3-dimethylbutanoyloxy)-13α-octanoyloxy-3*β*-hydroxyingenol	H	$CO(CH_2)_6CH_3$	OA	*E. esula*	133
418	3*β*,13α,17-tri-*O*-benzoyloxy-20-hydroxyingenol	Bz	Bz	OH	*E. esula*	133
419	13α,17-dibenzoyloxy-3*β*-*O*-(2,3-dimethylbutanoyloxy)-20-hydroxyingenol	A	Bz	OH	*E. esula*	133
420	3*β*,17-dibenzoyloxy-3α-*O*-(2,3-dimethylbutanoyloxy)-20-hydroxyingenol	Bz	A	OH	*E. esula*	133
421	13α-acetoxy-17-benzoyloxy-3*β*-*O*-(2,3-dimethylbutanoyloxy)ingenol	A	Bz	H	*E. esula*	133

afford a 5/6/5/5-ring system of paraliane **555**. Oxidation followed by ring expansion and acetylation leads to a pepluane **556**. 1(15→14) *Abeo*jatrophane skeleton (**212**−**214**) could be derived from **557** by pinacol rearrangement (Scheme 3).[43] This mechanism can be applied to the biosynthesis of lathyranone A (**261**).[95] The C2-unit of bishomojatrophanes (**192**−**208**) is to be from acetyl or malonyl thiol ester moieties (Scheme 4).[75]

3.2. Biosynthesis from Lathyranes

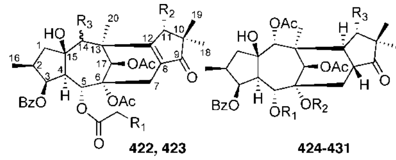
Three types of myrsinane diterpenoids and euphoractins would be formed from epoxy lathyranes (**558** or **559**) as shown in Scheme 5.[19] The rare 5/6/7/3-ring system of lagaspholone A (**324**), a jatropholane-type skeleton, is from lathyrane **560** (Scheme 6).[115] Lathyranoic acid (**260**) would be an oxidative degradation product of Euphorbia factor L_{11} (**252**) (Scheme 7).[91]

4. Biological Activity

4.1. Antiproliferative Activity

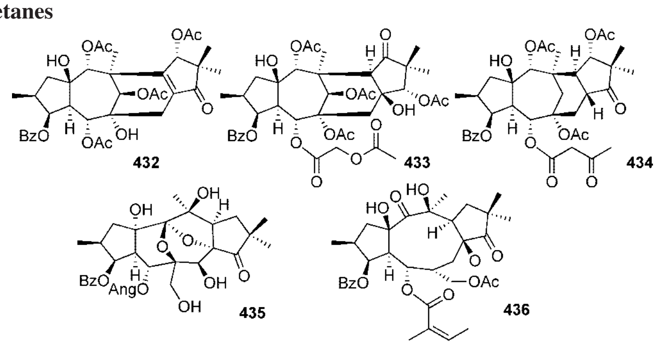
In 1997, Xu et al. reported that yuexiandajisu B (**57**) from *E. ebracteolata* inhibited proliferation of B lymphocytes *in vitro* preliminary bioassays.[42] Valente et al. reported the *in vitro* effect of pubescenol (**147**), helioscopinolide A (**20**), helioscopinolide B (**21**), and pubescene D (**170**) on the human tumor cell lines MCF-7 (breast adenocarcinoma), NCI-H460 (nonsmall cell lung cancer), and SF-268 (CNS cancer). All four of the compounds were shown to be moderate inhibitors of the growth of these cell lines.[26] Putranjivain A, a tannin extracted from the whole plant of *E. jolkini* Bioss, was reported to inhibit the proliferation of MCF-7 by blocking cell cycle progression in the G0/G1 phase and inducing apoptosis.[173] In 2005, Nishimura et al. reported the proliferation activity of acetone extract of the whole plants of *E. lunulata* for insulin- and interleukin-10 (IL-10)-dependent cell lines.[170] Fractionation of the active extract led to the isolation of quercetin 3-*O*-(2″,3″-digalloyl)-

Table 53. Segetanes-1



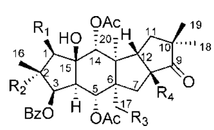
no.	name	R_1	R_2	R_3	plant	ref
422	segetene B	OAc	H	α-OAc	*E. paralias*	57
423	segetene A	H	OAc	*β*-OAc	*E. paralias*	57
424	(2 *S**,3 *S**,4 *R**,5 *R**,6 *R**,8 *R**,12 *S**,13 *R**,14 *R**,15 *R**)-6,14,17-triacetoxy-5-(2-acetoxyacetoxy)-3-benzoyloxy-15-hydroxysegetan-9-one	$COCH_2OAc$	Ac	H	*E. segetalis*	38
					E. paralias	59
425	(2 *S**,3 *S**,4 *R**,5 *R**,6 *R**,8 *R**,12 *S**,13 *R**,14 *R**,15 *R**)-6,11,14,17-tetraacetoxy-5-(2-acetoxyacetoxy)-3-benzoyloxy-15-hydroxysegetan-9-one	$COCH_2OAc$	Ac	OAc	*E. segetalis*	38
					E. paralias	59
426	(2 *S**,3 *S**,4 *R**,5 *R**,6 *R**,8 *R**,12 *S**,13 *R**,14 *R**,15 *R**)-6,14,17-triacetoxy-3-benzoyloxy-15-hydroxy-5-(2-hydroxyacetoxy)segetan-9-one	$COCH_2OH$	Ac	H	*E. segetalis*	38
					E. paralias	57
427	euphoportlandol B: 5α,11α,14α,17-tetraacetoxy-3*β*-benzoyloxy-6*β*,15*β*-dihydroxysegetan-9-one	Ac	H	OAc	*E. portlandica*	136
428	(2 *S**,3 *S**,4 *R**,5 *R**,6 *R**,8 *R**,11 *S**,12 *S**,13 *R**,14 *R**,15 *R**)-5,6,11,14,17-pentaacetoxy-3-benzoyloxy-15-hydroxysegetan-9-one	Ac	Ac	OAc	*E. paralias*	59
429	paralinone B	$COCH_2OAc$	Ac	OAc	*E. paralias*	137
430	paralinone A	$COCH_2OAc$	Ac	H	*E. paralias*	137
431	segetanin A	Ac	Ac	OH	*E. paralias*	138

Table 54. Segetanes-2 and Presegetanes



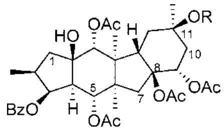
no.	name	plant	ref
432	euphoportlandol A: 5α,11α,14α,17-tetraacetoxy-3*β*-benzoyloxy-6*β*,15*β*-dihydroxy-seget-8(12)-en-9-one	*E. portlandica*	136
433	segetanin B	*E. paralias*	138
434	(2 *S**,3 *S**,4 *R**,5 *R**,6 *S**,8 *R**,11 *S**,12 *S**,13 *R**,14 *R**,15 *R**)-6,11,14-triacetoxy-3-benzoyloxy-15-hydroxy-5-(3-oxobutanoyl)-9-segetanone	*E. paralias*	59
435	(2 *S**,3 *S**,4 *R**,5 *R**,6 *R**,7 *S**,8 *R**,12 *R**,13 *S**,14 *R**,15 *R**)-5-angeloyloxy-3-benzoyloxy-6,14:8,14-diepoxy-7,13,15,17-tetrahydroxy-15-*epi*-presegetan-9-one	*E. segetalis*	38
436	presegetanin	*E. paralias*	138

Table 55. Paralianes

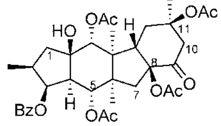


no.	name	R_1	R_2	R_3	R_4	plant	ref
437	(1 *R**,2 *R**,3 *S**,4 *R**,5 *R**,6 *R**,8 *S**,12 *S**,13 *S**,14 *R**,15 *R**)-1,5,8,14-tetraacetoxy-3-benzyloxy-15-hydroxyparalian-9-one	OAc	H	H	OAc	*E. segetalis*	38
						E. paralias	57
438	(1 *R**,2 *R**,3 *S**,4 *R**,5 *R**,6 *R**,8 *R**,12 *R**,13 *S**,14 *R**,15 *R**)-1,5,14-triacetoxy-3-benzoyloxy-15-hydroxyparalian-9-one	OAc	H	H	H	*E. segetalis*	38
439	(2 *R**,3 *R**,4 *S**,5 *R**,6 *R**,8 *R**,12 *R**,13 *S**,14 *R**,15 *R**)-2,5,14-triacetoxy-3-benzoyloxy-15-hydroxyparalian-9-one	H	OAc	H	H	*E. segetalis*	38
440	(1 *R**,2 *R**,3 *S**,4 *R**,5 *R**,6 *R**,8 *R**,12 *R**,13 *S**,14 *R**,15 *R**)-1,5,14,17-tetraacetoxy-3-benzoyloxy-15-hydroxyparalian-9-one	OAc	H	OAc	H	*E. segetalis*	38
441	(2 *S**,3 *S**,4 *R**,5 *R**,6 *R**,8 *S**,12 *S**,13 *S**,14 *R**,15 *R**)-5,8,14-triacetoxy-3-benzoyloxy-15-hydroxyparalian-9-one	H	H	H	OAc	*E. paralias*	59

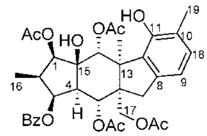
Table 56. Pepluanes



442 443



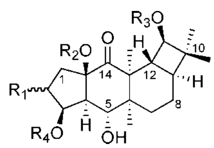
444



445

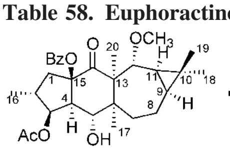
no.	name	R	plant	ref
442	(2 *S**,3 *S**,4 *R**,5 *R**,6 *R**,8 *R**,9 *R**,10 *R**,12 *S**,13 *S**,14 *R**,15 *R**)-5,8,9,11,14-pentaacetoxy-3-benzoyloxypepluan-15-ol	Ac	*E. peplus*	44
443	(2 *S**,3 *S**,4 *R**,5 *R**,6 *R**,8 *R**,9 *R**,10 *R**,12 *S**,13 *S**,14 *R**,15 *R**)-5,8,9,11,14-tetraacetoxy-3-benzoyloxypepluane-11,15β-diol	H	*E. peplus*	139
444	pepluanone	–	*E. peplus*	140
445	(1 *S**,2 *R**,3 *S**,4 *R**,5 *R**,6 *R**,13 *S**,14 *R**,15 *R**)-1,5,14,17-tetraacetoxy-3-benzoyloxy-8,10,(18)11-hexadehydropepluane-11,15-diol	–	*E. segetalis*	38

Table 57. Euphoractines-1

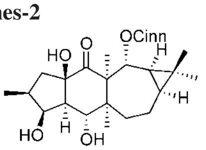


no.	name	R_1	R_2	R_3	R_4	plant	ref
446	3β-acetoxy-11β-methoxyeuphoractine D	α-Me	Bz	CH_3	Ac	*E. villosa*	87
447	3β-acetoxy euphoractine D	α-Me	Bz	H	Ac	*E. villosa*	87
448	euphoractine A	β-Me	Cinn	H	H	*E. micractina*	141
449	euphoractine C	β-Me	Bz	H	H	*E. micractina*	142
450	euphoractine D	α-Me	Bz	H	H	*E. micractina*	142

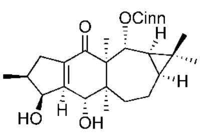
Table 58. Euphoractines-2



451



452



453

no.	name	plant	ref
451	no name	*E. villosa*	86
452	euphoractine B	*E. micractina*	141
453	euphoractine E	*E. micractina*	142

β-D-galactopyranoside (**544**), quercetin 3-*O*-(2″-galloyl)-β-D-galactopyranoside (**545**), quercetin, and gallic acid. Compounds **544** and **545** showed proliferation activity for BAF/InsR (insulin-dependent cell line), whereas quercetin and gallic acid showed stronger proliferation activity for BAF/IL10R than compounds **544** and **545**.[170]

4.2. Cytotoxicity

Lathyrane diterpenoids **228**, **229**, and **234**, isolated from *E. nivulia*, showed significant cytotoxic activity against Colo 205, MT2, and CEM cell lines. The LD_{50} values are almost the same in the three cell lines for the three compounds.[84] 17-Acetoxyjolkinolide B (**13**) and 13-hexadecanoyloxy-12-deoxyphorbol (**339**), obtained from the dried roots of *Euphorbia fischeriana,* exhibited potent cytotoxic activity to Ramos B cells with IC_{50} values of 0.023 and 0.0051 μg/mL, respectively.[21] Daphnane diterpenoids **326**, **327**, and tigliane diterpenoids **342**–**345**, isolated from the bioactivity-guided fractionation of the latex of *E. poisonii*, showed strong cytotoxic selectivity for the human kidney carcinoma (A-498) cell line with potencies exceeding that of adriamycin by 10 000 times.[123] Compound **235**, also from *E. poisonii*,[85] modestly cytotoxic against A-549, MCF-7, HT, A-498, PC-3, and PACA-2, exhibited nonselective ED_{50} values ranging from 2 to 4 μg/mL, whereas **237** was weakly but selectively active at ED_{50} 15 μg/mL against the prostate adrenocarcinoma (PC-3).[85]

4.3. Effects on the Cell Division

Ingenane-type diterpenoids **360**–**368**, **382**, **383**, **399**–**404**, and euphane triterpenoids **454**–**457**, all isolated from *E. kansui*,[62,65,135,143] showed significant effects on the cell diversion of *Xenopus laevis* cells at the blastular stage. **360**–**368**, **382**, and **383** arrested cleavage significantly (0.5 μg/mL of each compound resulted in >75% and 60% cleavage arrest, respectively). **402**, **403**, and **454**–**457** showed some activity (10 μg/mL of each compound resulted in >60% and >50% cleavage arrest, respectively).

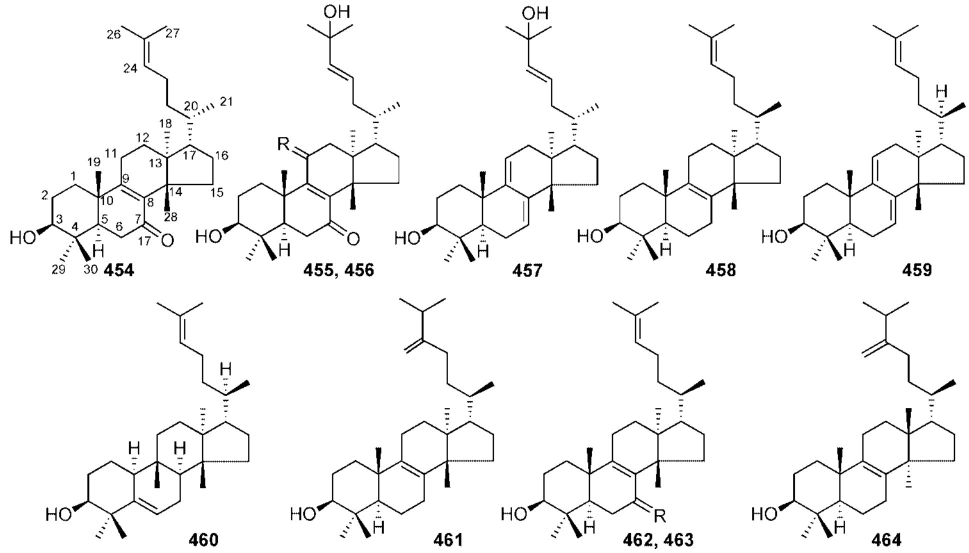
4.4. DNA-Damaging Activity

In a mutant yeast bioassay, compound **293**, isolated from *E. decipiens*, showed a positive response to DNA-damaging activity with IC_{12} values of 750 μg/mL against RS322Y (rad 52) and 1090 μg/mL against wild-type LF 15 (Rad+).[105] Camptothecin was used as the standard drug, with IC_{12} values of 12 μg/mL for the mutant strain (rad 52) and 75 μg/mL for the wild type.

4.5. Modulatority of Multidrug Resistance

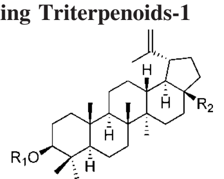
In a rhodamine 123 exclusion test using L5178 mouse lymphoma cells, euphosalicin (**216**) was found to be more active than verapamil in reversing multidrug resistance in mouse lymphoma cells.[63] The jatrophane diterpenoids **92**, **112**, and **151**, isolated from *E. mongolica*, also demonstrated a concentration-dependent effect in inhibiting the efflux pump activity of the tumor cells in the range 11.2–112 μM.[49] Jatrophane diterpenoids **61**, **64**, and **119** (*E. peplus*), as well as two segetane diterpenoids, euphoportlandols B (**427**) and A (**432**) (*E. portlandica*), were found to be inhibitors of P-glycoprotein in the same test.[66,136,115] The

Table 59. 6/6/6/5 Ring Triterpenoids



no.	name	R	plant	ref
454	kansenone	–	*E. kansui*	143
455	kansenonol	H_2	*E. kansui*	143
456	11-oxo-kansenonol	O	*E. kansui*	143
457	kansenol		*E. kansui*	143
458	euphol		*E. antiquorum*	144
			E. aleppica	114
			E. kansui	143
459	antiquol C: eupha-7,9(11),24-trien-3β-ol		*E. antiquorum*	144
460	antiquol B: 19(10→9)*abeo*-8α(H),9β(H),10α (H)-eupha-5,24-dien-3β-ol		*E. antiquorum*	144
461	euphorbol: 24-methylenetirucall-8-en-3β-ol		*E. antiquorum*	144
462	*epi*-kansenone	O	*E. kansui*	143
463	lanosterol	H_2	*E. peplus*	145
464	24-methylenelanosterol		*E. peplus*	145

Table 60. 6/6/6/6/5-Ring Triterpenoids-1



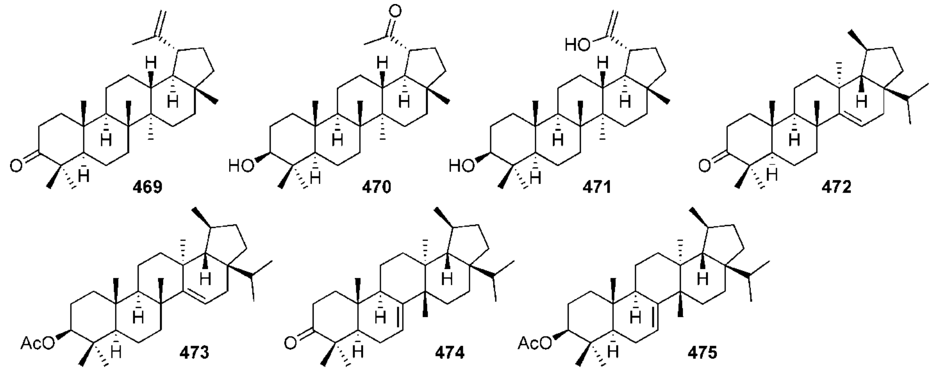
no.	name	R_1	R_2	plant	ref
465	lupeol acetate	Ac	Me	*E. altotibetic*	52
				E. quinquecostata	30
				E. stygiana	146
466	betulin	H	CH_2OH	*E. latifolia*	147
				E. myrsinites	104
467	betulinic acid	H	COOH	*E. latifolia*	147
468	lupeol	H	Me	*E. humifusa*	148
				E. chamaesyce	149

macrocyclic lathyrane polyester Euphorbia factor L_{10} (**253**) showed powerful inhibition of the transport activity of P-glycoprotein in the experiment using one million K562/R7 human leukemic cells expressing high levels of P-glycoprotein.[92]

Corea et al. studied on the structure–activity relationships of jatrophane diterpenoids as modulators of multidrug resistance. In 2003, they isolated a series of 10 closely related jatrophanes **102** and euphodendroidins A-I (**103-111**) from the Mediterranean spurge *E. dendroides* L., which served as a base for the establishment of structure–activity relationships within this class of P-glycoprotein inhibitors.[51] The efficiency of euphodendroidins to inhibit P-glycoprotein-mediated daunomycin efflux was investigated by monitoring the intracellular accumulation of this drug. The results demonstrated the critical role of a free hydroxy at C-3, lacking of oxygenation at C-2 and the differential effect of substituent at C-5. Hydroxylation or acyloxylation at this C-2 was detrimental for the activity. The nicotinoyl derivative euphodendroidin C (**105**) was 2-fold less active compared to its 2-methylbutanoyl and isobutyryl analogs. The most powerful compound of the series, euphodendroidin D (**106**), outperformed cyclosporin by a factor of 2 to inhibit Pgp-mediated daunomycin transport. They also got 12 compounds, terracinolides B, C, H, J, K, L, 13α-OH terracinolides B, F, G, *abeo*dendroidin F, and *epi-abeo*dendroidin F (**193**, **194**, **199–205**, **213**, and **214**) from *E. dendroides* L.[74] All of the compounds were tested as inhibitors of the drug-efflux activity of P-glycoprotein from cancer cells. The main information was that the revertant activity of terracinolides and abeojatrophanes was strongly affected by the presence of a free hydroxy group, with the following ranking of position: 3 < 15 < 13 < 2. In addition, substitution at position 6 affected the inhibitory ability in a way that dramatically depends on the location of the free hydroxy group. These observations suggest that jatrophanes and modified jatrophanes share a common gross pharmacophore, which is dramatically affected by changes of the oxygenation pattern.

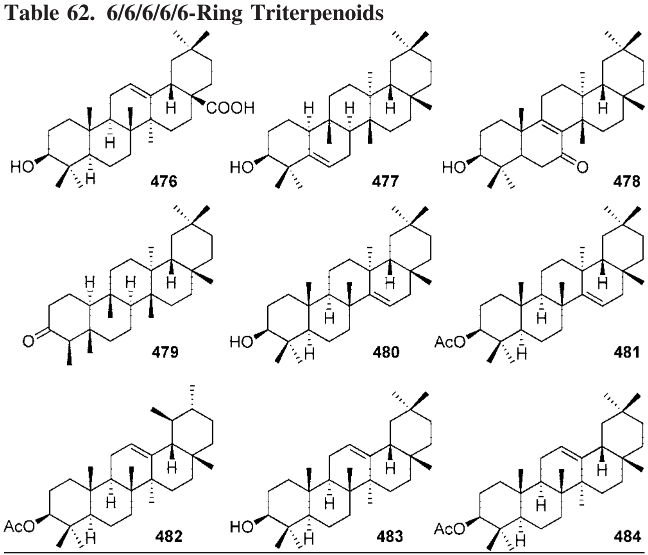
In 2004, Corea et al. went on researching the same structure–activity relationships.[45] The main object was to reveal the importance of substitutions on the medium-sized

Table 61. 6/6/6/6/5-Ring Triterpenoids-2



No.	name	plant	ref
469	lupenone	*E. segetalis*	150
		E. stygiana	146
470	3*β*-hydroxy-30-*nor*-lupan-20-one	*E. chamaesyce*	149
471	lup-20(30)-ene-3*β*,29-diol	*E. chamaesyce*	151
472	D-friedomadeir-14-en-3-one	*E. mellifera*	152
		E. stygiana	146
473	D-friedomadeir-14-en-3*β*-yl acetate	*E. stygiana*	146
474	D:C-friedomadeir-7-en-3-one	*E. mellifera*	152
		E. stygiana	146
475	D:C-friedomadeir-7-en-3*β*-yl acetate	*E. stygiana*	146

Table 62. 6/6/6/6/6-Ring Triterpenoids



no.	name	plant	ref
476	oleanolic acid	*E. latifolia*	147
477	glutinol	*E. chamaesyce*	153
		E. segetalis	150
478	3*β*-hydroxymultiflor-8-en-7-one	*E. chamaesyce*	153
479	friedeline	*E. segetalis*	130
480	taraxerone	*E. pubescens*	26
		E. stygiana	146
481	taraxeryl acetate	*E. stygiana*	146
482	α-amyrin acetate	*E. ebracteolata*	20
483	*β*-amyrin	*E. ebracteolata*	154
484	*β*-amyrin acetate	*E. ebracteolata*	154
		E. fischeriana	155

ring (carbons 8, 9, 14, and 15). Through the insight of seven jatrophane diterpenoids, pepluanins A−E (**66**−**68**, **86**, and **87**), **11**, and **65**, isolated from *E. peplus* L., they found that the activity was collapsed by the presence of C-8 hydroxy, whereas it increased with C-14 carbonyl, C-9 acetoxy, and C-15 hydroxy groups. Pepluanin A (**66**) showed a very high activity for a jatrophane diterpenoid, outperforming cyclosporin A by a factor of at least 2 in the inhibition of Pgp-mediated daunomycin transport.

4.6. Tumor Promoting Activity

Diterpene esters of the phorbol and ingenol types are known to be highly active tumor promoting agents that typically occur in members of the Euphorbiaceae.[128] Latex as well as total leaf extracts of *E. leuconeura* exhibited Epstein−Barr-virus (EBV) inducing activity comparable to TPA (12-*O*-tetradecanoylphorbol acetate), a well-known tumor promoter. The activity of individual fractions correlated with their ingenol ester content.[128] Compounds **391**−**397**, obtained from the latex of *E. cauducifolia*, were evaluated for cocarcinogenic and tumor-promoting activity on the back skin of NMRI mice. After 24 weeks, an average tumor rate of 7% and an average tumor yield of 0.07 tumors/mouse were noticed. After 36 weeks, an average tumor rate of 36% was observed and the average tumor yield was 0.45 tumors/mouse.[130]

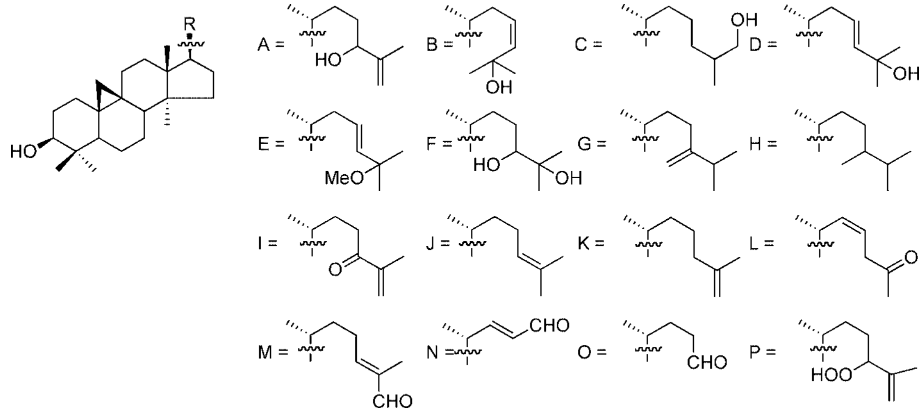
4.7. Pro-Inflammatory Activity

In 1999, Hohmann et al. investigated the irritant activities of some jatrophane diterpenes isolated from *E. peplus*. Only compound **77** was found to exert a weak pro-inflammatory activity on mouse ear of $ID_{50}^{4} = ID_{50}^{24} = 29$ μg/ear (the redness of the mouse ear was estimated 4 and 24 h after the application of solutions in Me_2CO). These data indicated that this type of diterpene does not play a significant role in the skin irritant activity of *Euphorbia* species.[55]

4.8. Inhibition of Allergic Reactions

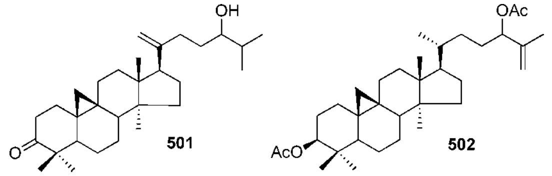
The water soluble fraction of *E. royleana* latex, showed dose-dependent anti-inflammatory and antiarthritic effects in different acute and chronic test models in rats and mice. It reduced the exudate volume and the migration of leukocytes and showed poor inhibitory effect on the granuloma formation induced by cotton pellets, while it had a low ulcerogenic score. The oral LD_{50} was more than 1500 mg/kg in both of rats and mice.[174] Oral administration of petroleum ether extract of the aerial parts of *E. splendens* caused significant inhibition of edema and produced inhibition of leucocyte migration and exudate volume in the affected tissues. The

Table 63. Cycloartanes-1



no.	name	R	plant	ref
485	cycloart-25-ene-3β,24-diol	A	*E. sessiliflora*	15
			E. myrsinites	104
			E. portlandica	136
			E. aleppica	113
			E. altotibetic	52
			E.humifusa	148
486	cycloart-23*Z*-ene-3β,25-diol	B	*E. sessiliflora*	15
			E. portlandica	136
			E.humifusa	148
			E. chamaesyce	153
487	cycloartane-3β,26-diol	C	*E. portlandica*	136
488	cycloart-23*E*-ene-3β,25-diol	D	*E.humifusa*	148
			E. myrsinites	104
			E. altotibetic	52
489	25-methoxycycloart-23*E*-en-3β-ol	E	*E. sessiliflora*	15
490	cycloartane-3β,24,25-triol	F	*E. sessiliflora*	15
			E. portlandica	136
491	24-methylenecycloartan-3β-ol	G	*E. myrsinites*	104
			E. aleppica	113
			E. portlandica	136
			E. segetalis	150
			E. peplus	148
			E. pubescens	26
			E. ebracteolata	154
492	cyclolaudanol	H	*E. myrsinites*	104
			E. aleppica	113
493	3β-hydroxy-cycloart-25-en-24-one	I	*E. myrsinites*	104
			E. portlandica	136
			E. aleppica	113
494	cycloartenol	J	*E. peplus*	145
			E. neriifolia	156
			E. segetalis	150
495	cycloart-25-en-3β-ol	K	*E. nivulia*	80
496	27-*nor*-3β-hydroxycycloartan-25-one	L	*E. portlandica*	136
497	(24*E*)-3β-hydroxycycloart-24-en-26-al	M	*E. portlandica*	136
498	(22*E*)-25,26,27-tri*nor*-3β-hydroxycycloart-22-en-24-al	N	*E. portlandica*	136
499	25,26,27-tri*nor*-3β-hydroxycycloartan-24-al	O	*E. portlandica*	136
500	24-hydroperoxycycloart-25-en-3β-ol	P	*E. portlandica*	136

Table 64. Cycloartanes-2



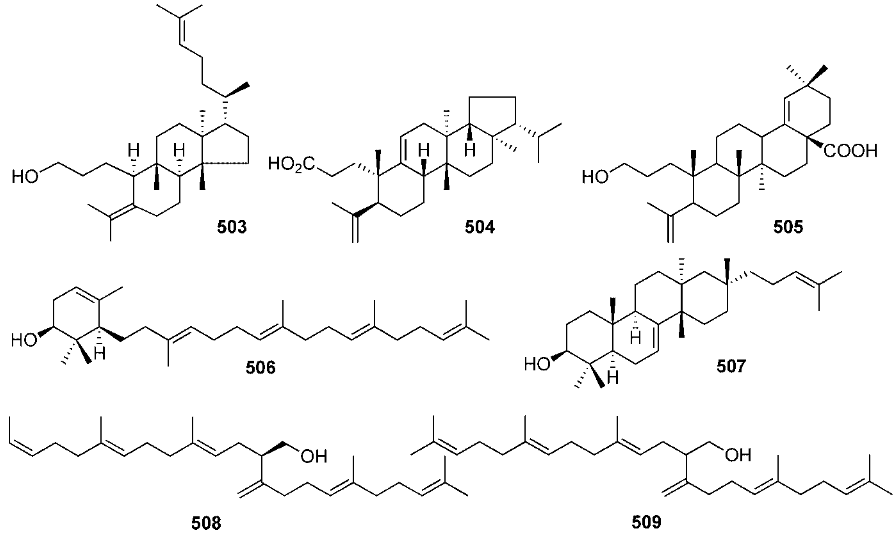
no.	name	plant	ref
501	neriifolione	*E. neriifolia*	156
502	3β,24-diacetoxycycloart-25-ene	*E. portlandica*	136

oral LD_{50} in both rats and mice was approximately 1250 mg/kg.[175] A 95% ethanol extract from whole aerial parts of *E. hirta* (EH A001) showed antihistaminic, anti-inflammatory and immunosuppressive properties in various animal models.[176] *In vivo* tests, pepluanone (**444**), isolated from *E. peplus*, significantly reduced carrageenin-induced edema by 40% and 60%.[140] The lathyrane diterpenoid **229** showed significant PGE_2 inhibition using *in vitro* assay method employing Enzyme Immunoassay Kits. The IC_{50} value for compound **229** was found to be 0.003 μM compared to that of known PGE_2 inhibitor celecoxib (0.050 μM).[80]

4.9. Antimicrobial Activity

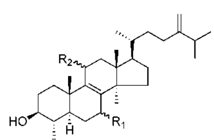
Ent-11β-hydroxyabieta-8(14),13(15)-dien-16,12α-olide (**16**) showed moderate to strong growth inhibition against *Bacillus cereus*, *B. subtilis*, *Micrococcus flavas*, *Moraxella catarrhalis*, *Neisseria sicca*, and *Candida albicans* CBS 5763 at 12.5 μg/mL concentration. Jolkinolide A (**9**) also moderately inhibited

Table 65. Secotriterpenoids and Others



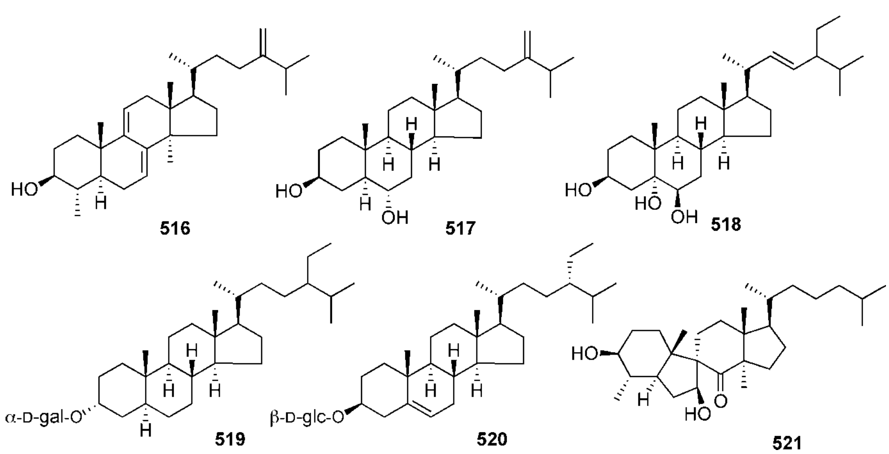
no.	name	plant	ref
503	isohelianol	*E. antiquorum*	144
504	3,4-*seco*-8β(H)-ferna-4(23),9(11)-dien-3-oic acid	*E. chamaesyce*	153
505	3,4-*seco*-oleana-4(23),18-dien-3-oic acid	*E. chamaesyce*	157
506	camelliol C	*E. antiquorum*	144
507	lemmaphylla-7,21-dien-3β-ol	*E. antiquorum*	144
508	peplusol	*E. peplus*	145
509	anhydrobisfarnesol	*E. laterifiora*	158

Table 66. Steroids-1



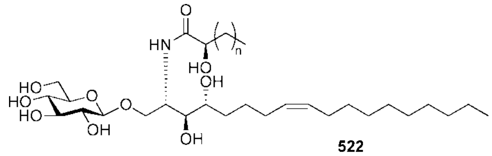
no.	name	R_1	R_2	plant	ref
510	3β-hydroxy-4α,14α-dimethyl-5α-ergosta-8,24(28)-dien-11-one	H_2	=O	*E. chamaesyce*	151
511	3β,11α-dihydroxy-4α,14α-dimethyl-5α-ergosta-8,24(28)-dien-7-one	=O	α-OH	*E. chamaesyce*	151
512	3β,7α-dihydroxy-4α,14α-dimethyl-5α-ergosta-8,24(28)-dien-11-one	α-OH	=O	*E. chamaesyce*	151
513	3β-hydroxy-4α,14α-dimethyl-5α-ergosta-8,24(28)-dien-7-one	=O	H_2	*E. chamaesyce*	149
514	3β-hydroxy-4α,14α-dimethyl-5α-ergosta-8,24(28)-dien-7,11-one	=O	=O	*E. chamaesyce*	149
515	obtusifoliol	H_2	H_2	*E. chamaesyce*	149

Table 67. Steroids-2



no.	name	plant	ref
516	4α,14α-dimethyl-5α-ergosta-7,9(11),24(28)-trien-3β-ol	*E. chamaesyce*	149
517	5α-stigmastane-3β,6α-diol	*E. boetica*	111
518	5α-stigmastane-3β,5,6β-triol	*E. boetica*	111
519	geniculatoside F	*E. geniculata*	159
520	3-(β-D-glucopyranosyloxy)stigmast-5-ene	*E. peplis*	160
521	(3 *S*,4 *S*,5 *R*,7 *S*,9 *R*,14 *R*)-3,7-dihydroxy-4,14-dimethyl-7(8→9) *abeo*cholestan-8-one	*E. officinarum*	86

Table 68. Cerebrosides.



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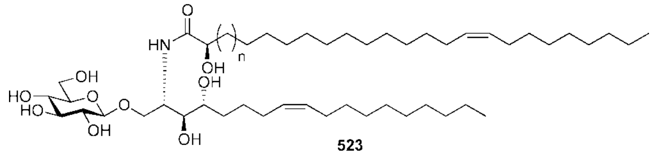
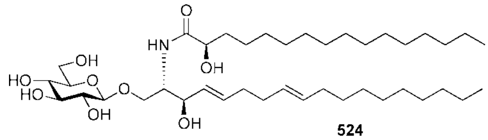


523



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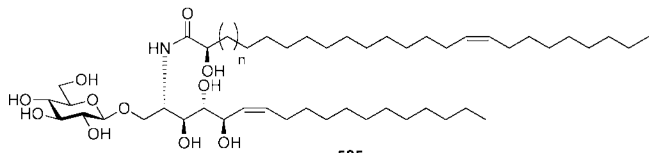
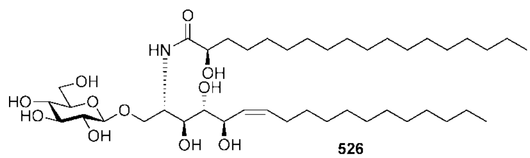
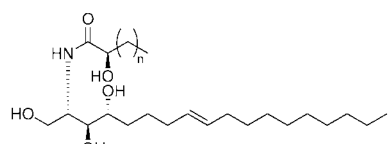


525



526

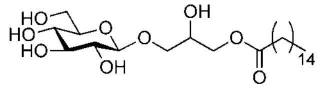


527

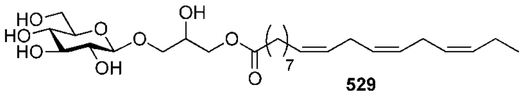
no.	name	*n*	plant	ref
522	(2 *S*,3 *S*,4 *R*,8 *Z*)-1-*O*-(β-D-glucopyranosyl)-2-[(2′ *R*)-2′-hydroxy(icosanoyl~octacosanoyl)amino]-8-octadecene-1,3,4-triol	17	*E. nicaeensis*	161
		19,20	*E. sororia*	162
		21	*E. peplis*	163
			E. nicaeensis	161
			E. sororia	162
		22~25	*E. sororia*	162
523	(2 *S*,3 *S*,4 *R*,8 *Z*)-1-*O*-(β-D-glucopyranosyl)-2-[(2′ *R*,15′ *Z*)-2′-hydroxy(tetracos-15′-enoyl~octacos-19′-enoyl)amino]-8-octadecene-1,3,4-triol	1	*E. peplis*	163
			E. characias	164
			E. wulfenii	165
		3	*E. peplis*	163
			E. characias	164
			E. wulfenii	165
		5	*E. wulfenii*	165
524	(2 *S*,3 *S*,4 *E*,8 *E*)-1-*O*-(β-D-glucopyranosyl)-2-[(2′ *R*)-2′-hydroxyhexadecanoylamino]-4,8-octadecadiene-1,3-diol	−	*E. peplis*	163
525	(2 *S*,3 *S*,4 *R*,5 *R*,6 *Z*)-1-*O*-(β-D-glucopyranosyl)-2-[(2′ *R*,15′ *Z*)-2′-hydroxy(tetracos-15′-enoyl~octacos-19′-enoyl)amino]-6-octadecene-1,3,4,5-tetraol	1	*E. characias*	166
		3	*E. characias*	166
		5	*E. characias*	166
526	(2 *S*,3 *S*,4 *R*,5 *R*,6 *Z*)-1-*O*-(β-D-glucopyranosyl)-2-[(2′ *R*)-2′-hydroxyoctacosanoylamino]-6-octadecene-1,3,4,5-tetraol	−	*E. characias*	166
527	(2 *S*,3 *S*,4 *R*,8 *E*,2′ *R*)-2-(2′-hydroxyeicosanoyl~hexacosanoylamino)-8-octacecene-1,3,4-triol	17~23	*E. sororia*	162

the growth of *M. catarrhalis* at 50 μg/mL concentration.[15] Helioscopinolide A (**20**) and helioscopinolide B (**21**) showed significant activity against *Staphylococcus aureus* 6538P (2.5 μg/spot).[26] *In vitro* bioassays showed that yuexiandajisu A (**56**) exhibited antibacterial activity.[42] A mixture of cerebrosides (**522**−**524**) from *E. peplis*[163] showed a synergistic antifungal activity against *Candida* spp. and *Cryptococcus neoformans* strain. Moreover, only a single compound **523** (n = 3) showed an interesting antitubercular activity with MIC of 40 μg/mL on reference strain and on two clinical isolates and a MIC of 80 μg/mL against clinical strain H242. Natarajan et al. researched the antibacterial activity of *E. fusiformis* against pathogenic strains of Gram positive (*Bacillus subtilis* and *S. aureus*) and Gram negative bacteria (*Escherichia coli*, *Klebsiella pneumoniae*, *Proteus vulgaris*, *Pseudomonas aeruginosa*, *Salmonella typhii* A, and *S. typhii*

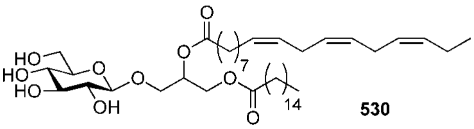
Table 69. Glycerols



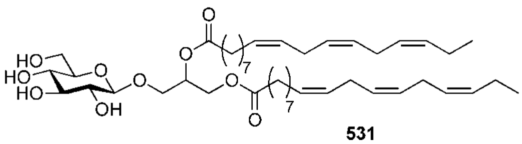
528



529



530



531

no.	name	plant	ref
528	1-*O*-(*β*-D-glucopyranosyl)-3-hexadecanoylglycerol	*E. cyparissias*	167
529	1-*O*-(*β*-D-glucopyranosyl)-3-(octadeca-9′ *Z*,12 *Z*′,15′ *Z*-trienoyl)glycerol	*E. peplis*	168
530	1-*O*-(*β*-D-glucopyranosyl)-3-hexadecanoyl-2-(octadeca-9′ *Z*,12′ *Z*,15′ *Z*-trienoyl)glycerol	*E. cyparissias*	167
531	1-*O*-(*β*-D-glucopyranosyl)-2,3-di(octadeca-9′ *Z*,12′ *Z*,15′ *Z*-trienoyl)glycerol	*E. cyparissias*	167

B).[177] The different extracts differed significantly in their antibacterial properties with the methanolic extract being very effective followed by acetone and chloroform extracts. Aqueous and ethanolic extract showed the very least activity. Rootstock extracts had better antibacterial properties than leaf extracts. The results of this study supported the use of this plant in traditional medicine to treat fever, wound infections, and intestinal disorders.[177] The ethanolic extracts of aerial parts of *E. hirta* exhibited a broad spectrum of antimicrobial activity against *E. coli*, *P. vulgaris*, *P. aeruginosa*, and *S. aureus*.[178]

Compound **438**, isolated from *E. paralias,* showed a moderate antiviral activity (EC_{50} = 14 mg/mL) against HIV-1 replication. The activity was based on the inhibition of virus-induced cytopathicity in MT-4 cells.[57] The 7 triterpenes (**458**−**461**, **503**, **506**, and **507**) isolated from *E. antiquorum* were examined for the inhibitory effects on Epstein−Barr virus early antigen (EBV-EA) activation induced by TPA. In this assay, compounds **458**−**461** and **503** showed 100% inhibition of activation at 1000 mol ratio/TPA.[144] The steroids **510**−**516**, isolated from *E. chamaesyce*, also exhibited potent inhibitory effects (100% inhibition of induction at 1000 mol ratio/TPA, about 80% inhibition at 500 mol ratio/TPA, and about 30% inhibition at 100 mol ratio/TPA) in the same assay. Compound **512** showed the most potent inhibitory effects in comparison to oleanolic acid on EBV-EA activation.[151]

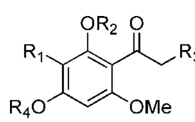
4.10. Antidiarrheal Activity

A significant antidiarrheal effect of the *E. paralias* extracts against castor oil-induced diarrhea in rats was achieved by 400 mg/kg.[179] It decreased the gastrointestinal movement as indicated by the significantly ($p < 0.01$) decreased distance traveled by the charcoal meal. The large dose of the extract was slightly more effective than the small one. The antidiarrheal effect was also evaluated on the motility of duodenum isolated from freshly slaughtered rabbits. The *E. paralias* methanol extract produced a transient stimulation followed by inhibition in doses of less than 0.05 mg/kg. Higher concentrations caused rapid muscle relaxation. Tannins, flavonoids, unsaturated sterols/triterpenoids, carbohydrates, lactones and proteins/amino acids were reported as major active constituents of the tested plants.[179] In 2006, Hore et al. reported the aqueous leaf extract of *E. hirta* decreased the gastrointestinal motility in normal rats and decreased the effect of castor oil-induced diarrhea in mice by 300 and 1000 mg/kg.[180]

4.11. Antipyretic-Analgesic Activity

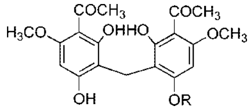
Myrsinane **266**, isolated from *E. decipens* whole plant chloroform extract, showed significant analgesic activity when administered to mice at dose of 5−20 mg/kg i.p. This activity is comparable to that of 100 mg/kg of aspirin or ibuprofen.[181] Resiniferatoxin (**326**), an ultrapotent capsaicin analog present in the latex of *E. resinifera*, interacts at a specific membrane recognition site, expressed by primary sensory neurons mediating pain perception as well as neurogenic inflammation. Desensitization to **326** is a promising approach to mitigate neuropathic pain and other pathological conditions in which sensory neuropeptides released from capsaicin-sensitive neurons play a crucial role.[182] Prostratin (**340**), obtained in *E. fischeriana*, showed significant analgesic and sedative activities. The 92% and 62% inhibitions were observed in sedative experiments with 20 mg/kg (p.o.) and 1 mg/kg (s.c.) in mice, respectively.[8] The ethyl acetate

Table 70. Phenolics-1



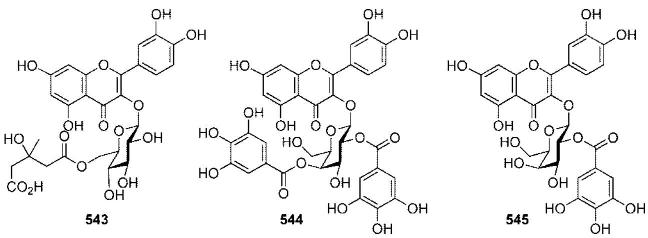
no.	name	R_1	R_2	R_3	R_4	plant	ref
532	2-hydroxy-4,6-dimethoxyacetophenone	H	H	H	Me	*E. portulacoides* *E. quinquecostata*	16 30
>**533**	2,4,6-trimethoxyacetophenone	H	Me	H	Me	*E. portulacoides*	16
534	2-hydroxy-4,6-dimethoxy-3-methylacetophenone	Me	H	H	Me	*E. portulacoides*	16
535	2,4,6-trimethoxy-3-methylacetophenone	Me	Me	H	Me	*E. portulacoides*	16
536	2,2′-dihydroxy-4,6-dimethoxy-3-methylacetophenone	Me	H	OH	Me	*E. quinquecostata*	30
537	2,4-dihydroxy-6-methoxyacetophenone	H	H	H	H	*E. fischeriana*	13
538	2,4-dihydroxy-6-methoxy-3-methylacetophenone	Me	H	H	H	*E. ebracteolata*	168
539	2-hydroxy-6-methoxy-3-methylacetophenone 4-*β*-D-glucopyranoside	Me	H	H	glc	*E. ebracteolata*	168
540	ebractelatinoside C	Me	H	H	glc→xyl(6→1)	*E. ebracteolata*	168

Table 71. Phenolics-2



no.	name	R	plant	ref
541	1,1-bis(2,6-dihydroxy-3-acetyl-4-methoxyphenyl)methane	H	*E. ebracteolata*	168
542	ebractelatinoside B	glc	*E. ebracteolata*	168

Table 72. Flavonoids



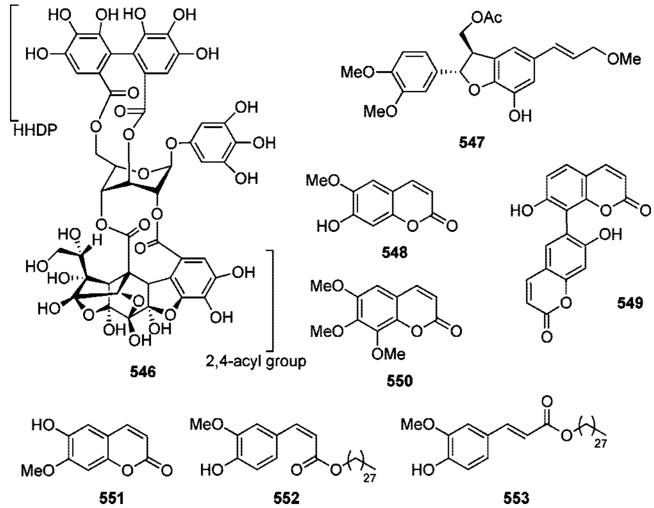
no.	name	plant	ref
543	quercetin 3-*O*-6′-(3-hydroxy-3-methylglutaryl)-β-D-glucopyranoside	*E. ebracteolata*	169
544	quercetin 3-*O*-(2″,3″-digalloyl)-β-D-galactopyranoside	*E. lunulata*	170
545	quercetin 3-*O*-(2″-galloyl)-β-D-galactopyranoside	*E. lunulata*	170

fraction from the residue of an 85% ethanol extract of the latex of *E. royleana* showed a dose related peripheral analgesic effect. The same fraction exhibited a significant antipyretic effect in hyperthermic rats and rabbits. The oral LD_{50} was more than 2 g/kg in rats and mice.[183] Following an identified use of the plant as analgesic in traditional medicine, the hexane, chloroform and ethyl acetate extracts of *E. heterophylla* root were tested for antinociceptive activity in rats. All extracts showed significant effects at doses of 150/300 mg/kg.[184]

4.12. Molluscicidal and Antifeedant Activities

In 2001 and 2002, Abdelgaleil et al. reported the molluscicidal and antifeedant activities of diterpenoids from *E. paralias*.[57,185] Compounds **132**, **437**, and particularly **441** had high molluscicidal activities on *Biomphalaria alexandrina*. Antifeedant activity was tested by a conventional leaf disk method against third-instar larvae of *Spodoptera littoralis*.[185] Compounds **142** and **426** were good insect antifeedants with 66.8 and 45.8% antifeedant activity (1000 mg/mL), respectively. Kansenonol (**455**) and **143** were moderately active at 500 ppm, whereas compounds **132**, **144**, **424**, **428**, **437**, and **438** showed moderate activity at 500−1000 ppm.[57] In 2004, Singh et al. reported the aqueous and serially purified latex extracts of plants *E. pulcherima* and *E. hirta* had potent molluscicidal activity.[186] Sublethal doses (40 and 80% of LC_{50}) of aqueous and partially purified latex extracts of both the plants also significantly altered the levels of total protein, total free amino acid, nucleic acid (DNA and RNA), and the activity of enzyme protease and acid and alkaline phosphatase in various tissue of the snail *Lymnaea acuminata* in time and dose dependent manner.

Table 73. Miscellaneous Compounds



no.	name	plant	ref
546	jolkinin	*E. jolkinii*	171
547	(−)-*trans*-9-acetyl-4,9′-di-*O*-methyl-3′-de-*O*-methyldehydrodiconiferyl alcohol	*E. quinquecostata*	36
548	scopoletin	*E. lunulata*	52
549	7,7′-dihydroxy-6,8′-bicoumarin (bicoumarol)	*E. quinquecostata*	36
550	6,7,8-trimethoxycoumarin	*E. quinquecostata*	30
551	6-hydroxy-7-methoxycoumarin (isoscopoletin)	*E. quinquecostata*	36
552	octacosyl *cis*-ferulate	*E. hylonoma*	172
553	octacosyl *trans*-ferulate	*E. hylonoma*	172

4.13. Inhibitory Activity on the Mammalian Mitochondrial Respiratory Chain

Six diterpenoids (**330**−**334** and **336**) isolated from the latex of *E. obtusifolia* were evaluated for their inhibition of the NADH oxidase activity in submitochondrial particles from beef heart.[187] 12,13-Diisobutyryloxy-4,20-dideoxyphorbol (**330**) was the most potent inhibitor and showed an inhibitory concentration with IC_{50} value of 2 0.6 ± 0 0.3 μM. In the study, some structure−activity trends were suggested for the inhibitory activity of the mammalian mitochondrial respiratory chain of the 4-deoxyphorbol esters, in which two isobutyryloxy groups were located at C-12 and C-13. Compound **330**, the strongest inhibitor of the NADH oxidase activity, had an unfunctionalized *gem*-dimethylcyclopropane moiety and C-20 was not oxygenated. Less active compounds, such as **333**, **334**, and **335**, C-17 (OAc), and C-20 (OH), were oxygenated.

4.14. Antidipsogenic Activity

The effect of the methanol extract obtained from the leaves and stems of *E. hirta* on thirst was examined using Wistar rats.[188] Intraperitoneal administration of 10 mg/100 mg body wt of the extract significantly ($p < 0.05$) decreased the amount of water consumed by rats. This effect lasted for 2 h.

4.15. Survival Effect on Fibroblasts PGE_2 In hibition Activity

Kansuinin E (**156**), isolated from the roots of *E. kansui*, exhibited a specific survival effect on fibroblasts that expressed TrkA with an ED_{50} value of 0.23 μg/mL when compared with TrkB cells.[64] In contrast, kansuinins A (**184**), D (**186**), and F (**160**) enhanced the survival of both TrkA- and TrkB-expressing fibroblasts. TrkA is a high-affinity receptor for nerve growth factor. The survival of these cells was solely dependent on NGF treatment, and they normally died in the absence of NGF. The survival of TrkB-expressing cells was dependent on the presence of brain-derived neurotrophic factor (BDNF), a member of the neurotrophin family related to NGF.[189]

4.16. PEP Inhibitory Activity

Prolyl endopeptidase (PEP) is the only serine protease that is known to cleave a peptide substrate in the *C*-terminal side of a proline residue and plays an important role in the metabolism of peptide hormones and neuropeptides and is recognized to be involved in learning and memory.[190] Low molecular weight inhibitors of PEP have been reported in the literature, but the majority of these were synthetic.[191] Most of the natural PEP inhibitors isolated have been of microbial origin whereas PEP inhibitors from plants have rarely been investigated.[192] The myrsinol-type diterpenoids **276**, **291**, and **292**, isolated from *E. decipiens*, were active against PEP.[101,105] Compounds **276** and **291** showed IC_{50} of 3.2 and 10.5 μM, respectively, with the positive control of Bacitracin. Compound **292** exhibited an IC_{50} of 16.9 ± 1.3 μM, which was compared with the positive control of PEP (*Z*-Pro-prolinal, IC_{50} of 1.27 ± 0.01 μM).

4.17. Urease Inhibitory Activity

Studies on the enzyme inhibition have led to the discoveries of drugs. Urease inhibitors have recently attracted much attention as potential new antiulcer drugs. Unfortunately, only a few natural products with this activity have been discovered. In 2003, Ahmad et al. reported the isolation of decipinol ester A (**273**) from *E. decipiens*.[101] It was the first naturally occurring urease inhibitor.

4.18. Angiotensin Converting Enzyme Inhibiting Activitiy

The methanol extract obtained from the leaves and stems of *E. hirta* inhibited the activity of angiotensin converting enzyme (ACE) by 90 and 50% at 500 and 160 μg, respectively, using enzyme linked immunosorbent assay (ELISA).[188]

4.19. Other Activities

3,4-Dimethoxycinnamaldehyde, isolated from *E. quinquecostata*, was significantly active in the induction of quinone reductase (QR) in Hepa1c1c7 hepatoma cells and in the inhibition of the transformation of murine epidermal JB6 cells with a CD (concentration to double induction) value of 9.5 μg/mL (52.8 μM) (QR assay) and an IC_{50} value of 2.3 μg/mL (12.8 μM) (JB6 assay), respectively.[36] The water and ethanol extracts (50 and 100 mg/kg) of *E. hirta* produced time-dependent increase in urine output. Electrolyte excretion was also significantly affected by the plant extracts.[193] The water extract increased the urine excretion of Na^+, K^+, and HCO_3^-. In contrast, the ethanol extract increased the excretion of HCO_3^-, decreased the loss of K^+, and had little effect on renal removal of Na^+.

5. Conclusion

The genus *Euphorbia* is widespread all over the world. The diterpenoids with jatrophane, lathyrane, tigliane, ingenane, *ent*-abietane, and myrsinol skeletons are among the most studied diterpenoids isolated from *Euphorbia* plants. Other types of diterpenoids, such as segetane, paraliane, pepluane, euphoractine, *ent*-atisnae, *ent*-kaurane, and casbane, along with triterpenes, sesquiterpenoids, steroids, and flavonoids are also important components. The rare compounds are cerebrosides, ellagitannin, neolignan, and manoyloxide, which isolated from *E. characias*,[163] *E. jolkinii*,[171] *E. quinquecostata*,[36] and *E. segetalis*,[38] respectively. Also, several enzymes have been isolated from the Euphorbiaceae family. The present review shows the majority of the compounds isolated from *Euphorbia*. But the structures of very common compounds such as organic acids and aliphatic hydrocarbons are not given.

The biological research on *Euphorbia* species has supported the use of some plants in traditional medicines or revealed the new activities on modern pharmacological levels. The biological activity includes antiproliferative activity, modulability of multidrug resistance, cytotoxic activity, DNA-damaging activity, antivirus activity, PEP inhibitory activity, antidiarrheal activity, molluscicidal and antifeedant activities, antimicrobial activity, antiinflammatory activity, antipyretic-analgesic activity, inhibitory activity on the mammalian mitochondrial respiratory chain, PGE_2 inhibition activity, angiotensin converting enzyme inhibiting activitiy, antidipsogenic activity, survival effect on fibroblasts, inhibitory activity on urease, effects on the cell division, tumor promoting activity, etc.

The insight of structure−activity relationships study on jatrophane diterpenoids as modulators of multidrug resistance has given us more detailed information about the active core framework and substituents.[45,51,74] It could help fellow researchers to find more active P-glycoprotein inhibitors.

6. Acknowledgments

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