·综述·

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天然产物中木栓烷型三萜核磁共振波谱特征

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〔摘要〕对天然产物中发现的木栓烷型三萜化合物的^{13}C-NMR、^{1}H-NMR谱学特征进行综述，以期减少天然产物特别是木栓烷型三萜结构鉴定工作的盲目性和重复性，为进一步研究分析木栓烷型三萜提供经验借鉴。

〔关键词〕木栓烷型三萜；核磁波谱特征；^{13}C-NMR；^{1}H-NMR

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NMR Spectral Characteristics of Natural Friedelanes: A Review

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〔**Abstract**〕The friedelane-type triterpenoids from natural products were studied in this paper including their chemical structures and spectral characteristics of ^{13}C-NMR, ^{1}H-NMR, so as to provide reference for reducing the blindness and repeatability of structure identification, and contribute to reducing some difficulties in the structure identification of friedelane-type triterpenoids, and provide theoretical basis for further research and analysis of friedelane-type triterpenoids.

〔**Keywords**〕friedelane-type triterpenoids; NMR spectral characteristics; ^{13}C-NMR; ^{1}H-NMR

木栓烷型(friedelane type)三萜及其皂苷主要分布于卫矛科(Celastraceae)、翅子藤科(Hippocrateaceae)、大戟科(Euphorbiaceae)、大风子科(Flacourtiaceae)和藤黄科(Guttiferae/Clusiaceae)等植物中，卫矛科(Celastraceae)和翅子藤科(Hippocrateaceae)中尤为常见。现代药理学研究表明，该类化合物具有抗肿瘤、抗炎、抗-HIV、抗菌、抗白血病和抗氧化等药理活性作用[1-6]。早在20世纪70年代，药物化学等领域的专家学者就对其进行了热门研究。近年来，越来越多结构复杂、新颖的木栓烷型三萜被发现，因其具有良好的药理活性而一直成为天然产物研究的热点。

与其它天然产物研究一样，木栓烷型三萜及其苷类化合物分离纯化得到单体化合物后，更为重要的一步是其结构和构型的鉴定(结构表征)。常用的波谱学鉴定方法主要有UV、IR、NMR、MS、X-Ray及CD等，其中一维和二维NMR在三萜的解析中起着至关重要的作用。通过FAB-MS、ESI-MS、HRMS和MS-MS等质谱技术可准确测定木栓烷型三萜的分子量及相应的结构信息，一维和二维NMR综合分析可快速确定三萜苷元、糖和苷元的连接位置、糖链结构等信息，再综合UV、IR、CD等鉴定手段和该物质的理化性质，以及必要的文献查阅，可准确地推测出其平面和立体结构。

本文对1980-2015年已报道的246个木栓烷型三萜的^{13}C-NMR和^{1}H-NMR数据进行归纳总结，以期

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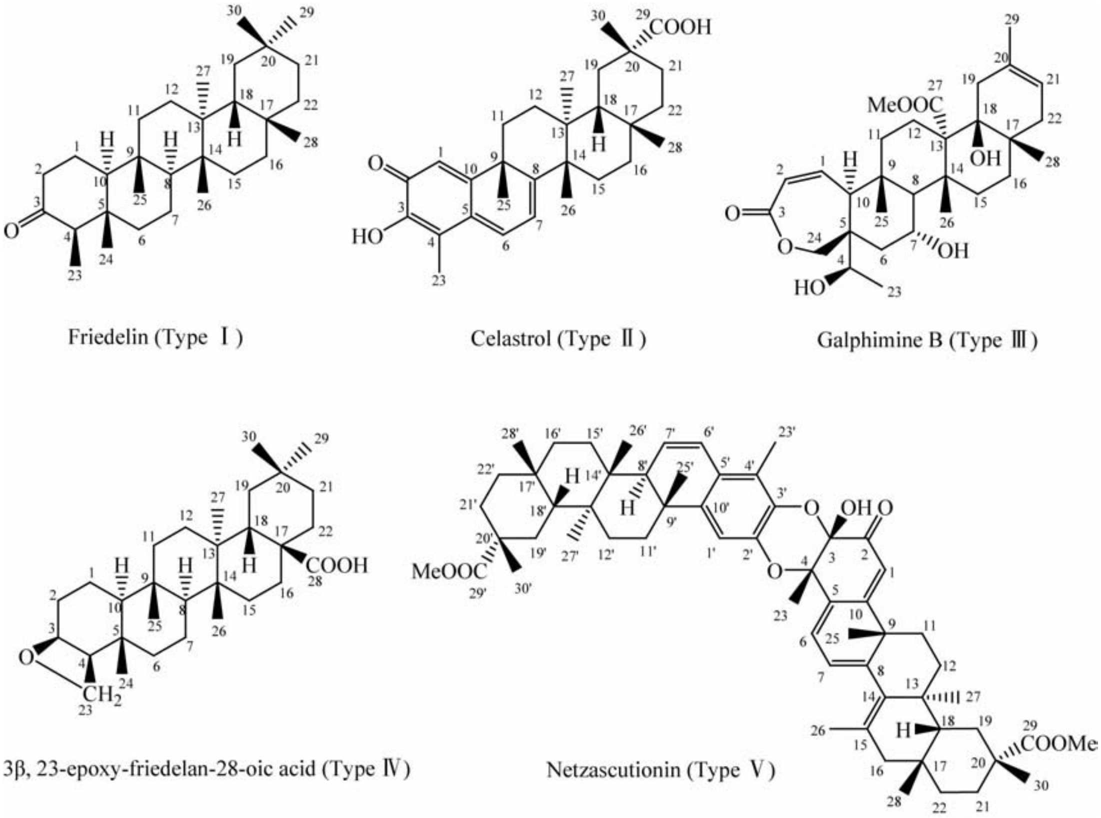
有助于相关研究者进行这类化合物的结构鉴定，为进一步分析研究木栓烷型三萜提供经验借鉴。

1 木栓烷型三萜的结构类型

天然产物中的木栓烷型三萜根据其结构特征主要分为5类：木栓烷型三萜(Intact friedelanes, Type Ⅰ)、降碳类木栓烷型三萜 (Norfriedelanes, Type Ⅱ)、开环型木栓烷型三萜 (Secofriedelanes, Type Ⅲ)、环氧型木栓烷型三萜 (Epoxyfriedelanes, Type Ⅳ)和二聚体类木栓烷型三萜(Dimers, Type Ⅴ)。从生物合成途径来看，木栓烷型三萜及其衍生物由角鲨烯-2,3-环氧化物的环化而得，在木栓烷型三萜的基本母核的结构基础上再进行碳环骨架的重排、转化、氧化和聚合，得降碳类、开环型、环氧型和二聚体类木栓烷型三萜及其衍生物。它们的基本结构类型和天然来源分别见图1和表1。



Friedelin (Type Ⅰ) Celastrol (Type Ⅱ) Galphimine B (Type Ⅲ)

3β, 23-epoxy-friedelan-28-oic acid (Type Ⅳ) Netzascutionin (Type Ⅴ)

图1 木栓烷三萜I–V类型的代表性化合物

表1 木栓烷型三萜的天然来源

化合物序号	化合物名称	天然来源（种）	所属科名	参考文献
I1	friedelin	*Kokoona zeylanica*	Celastraceae	[7]
I2	3,21-dioxofriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I3	3-oxo-21α-hydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I4	3-oxo-27-hydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I5	3,21-dioxo-27-hydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I6	3-oxo-21α,27-dihydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I7	3-oxo-6β-hydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I8	3,21-dioxo-6β-hydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I9	3-oxo-6β,21β-dihydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I10	3-oxo-6β,27-dihydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I11	3,21-dioxo-6β,27-dihydroxyfriedelane	*Kokoona zeylanica*	Celastraceae	[7,8]
I12	3,15-dioxofriedelane	*peritassa compta*	Celastraceae	[9]
I13	3-oxo-15α-hydroxyfriedelane	*peritassa compta*	Celastraceae	[9]
I14	1,3-dioxo-15α-hydroxyfriedelane	*peritassa compta*	Celastraceae	[9]
I15	1,3-dioxofriedelane	*peritassa compta*	Celastraceae	[9]
I16	3-oxo-30-hydroxyfriedelane	*Catha cassinoides*	Celastraceae	[10]
I17	3-oxo-29-hydroxyfriedelane	*Catha cassinoides*	Celastraceae	[10]
I18	3-oxofriedelan-29-oic acid	*Catha cassinoides*	Celastraceae	[10]
I19	3-oxo-25,28-dihydroxyfriedelane	*Elaeodendron glaucum*	Celastraceae	[11-13]

续表1

I20	3,22-dioxo-25-hydroxyfriedelane	*Elaeodendron glaucum*	Celastraceae	[11-13]
I21	3-oxofriedelan-25-al	*Elaeodendron glaucum*	Celastraceae	[11-13]
I22	3β-hydroxyfriedelane	*Elaeodendron glaucum*	Celastraceae	[11-13]
I23	3-oxo-25-hydroxyfriedelane	*Elaeodendron glaucum*	Celastraceae	[11-13]
I24	3-oxo-25-hydroxyfriedelan-28-al	*Elaeodendron glaucum*	Celastraceae	[11-13]
I25	3-oxo-28,29-dihydroxyfriedelane	*Elaeodendron balae*	Celastraceae	[14]
I26	3-oxo-friedelan-29-al	*Mortonia diffusa*	Celastraceae	[15]
I27	3β,29-dihydroxyfriedelane	*Mortonia diffusa*	Celastraceae	[15]
I28	3β,28-dihydroxyfriedelane	*Mortonia diffusa*	Celastraceae	[15]
I29	3,16-dioxofriedelane	*Maytenus diversifolia*	Celastraceae	[16-18]
I30	3,16,21-trioxo-6hydroxyfriedelane	*Maytenus diversifolia*	Celastraceae	[16-18]
I31	1,3-dioxo-28-hydroxyfriedelane	*Maytenus macrocarpa*	Celastraceae	[19]
I32	friedelan-3 α-ol	*Maytenus truncata Reiss*	Celastraceae	[20]
I33	3,11-dioxofriedelane	*Maytenus gonoclada* Mart.	Celastraceae	[21]
I34	3-oxo-12α-hydroxyfriedelane	*Maytenus gonoclada* Mart.	Celastraceae	[21]
I35	3,15-dioxo-21α-hydroxyfriedelane	*Maytenus robusta*	Celastraceae	[22]
I36	D:A-friedelan-24-al-3-en-3-ol-2-on-29-oic acid	*Maytenus ilicifolia*	Celastraceae	[23-24]
I37	D:A-friedelan-1-en-29-ol-3-one	*Maytenus ilicifolia*	Celastraceae	[23-24]
I38	2-oxo-3α,25-dihydroxyfriedelane	*Crossopetalum lobatum* Lundell	Celastraceae	[25]
I39	3-oxo-1β,25-dihydroxyfriedelane	*Crossopetalum lobatum* Lundell	Celastraceae	[25]
I40	3-oxo-2α-hydroxyfriedelan-30-oic acid	*Crossopetalum lobatum* Lundell	Celastraceae	[25]
I41	1,3-dioxo-28-hydroxy-friedelane	*Crossopetalum lobatum* Lundell	Celastraceae	[25]
I42	1,3-dioxo-29-hydroxyfriedelane	*Crossopetalum lobatum* Lundell	Celastraceae	[25]
I43	3-hydroxy-2-oxofriedelan-3-ene-20α-methylcarboxylate	*Austroplenckia populnea*	Celastraceae	[26-28]
I44	methyl populnonate	*Austroplenckia populnea*	Celastraceae	[26-28]
I45	3-hydroxy-2-oxofriedelan-3-ene-20α-carboxylic acid	*Austroplenckia populnea*	Celastraceae	[26-28]
I46	3β-hydroxy-2-oxofriedelan-20α-carboxylic acid	*Austroplenckia populnea*	Celastraceae	[26-28]
I47	28-hydroxyfriedelan-3-one-29-oic acid	*Euonymus hederaceus*	Celastraceae	[29]
I48	methyl-3-oxofriedelan-25-oate	*Euonymus hederaceus*	Celastraceae	[30]
I49	methyl friedelan-25-oate	*Euonymus hederaceus*	Celastraceae	[30]
I50	7-oxofriedelan-3α-yl acetate	*Euonymus hederaceus*	Celastraceae	[30]
I51	friedelan-2α,3α,28-triol	*Pristimera grahamii* A. C. Smith	Celastraceae	[31]
I52	friedelan-3α,28-diol	*Pristimera grahamii* A. C. Smith	Celastraceae	[31]
I53	3-hydroxy-2-oxo-D:A-friedoolean-3-en-29-oic acid	*Tripterygium wilfordii*	Celastraceae	[32]
I54	3β-hydroxy-D:B-friedoolean-5-en-29-oic acid	*Tripterygium wilfordii*	Celastraceae	[33]
I55	3β,29-dihydroxy-D:B-friedoolean-5-en	*Tripterygium wilfordii*	Celastraceae	[33]
I56	3-oxo-30-hydroxyfriedelan-28-al	*Tripterygium wilfordii*	Celastraceae	[34]
I57	3-oxo-30-hydroxy-friedelane formate	*Tripterygium wilfordii*	Celastraceae	[34]
I58	3-oxofriedelan-24-al-29-oic acid	*Tripterygium wilfordii* Hook f.	Celastraceae	[35]
I59	3-oxo-11β-hydroxyfriedelane	*Celastrus monospermus*	Celastraceae	[36-38]
I60	3-oxo-12β-hydroxyfriedelane	*Celastrus monospermus*	Celastraceae	[36-38]
I61	12β-hydroxyfriedelane-1-ene-3-one	*Celastrus monospermus*	Celastraceae	[36-38]
I62	21α-hydroxyfriedelane-1,3-dione	*Salacia verrucosa*	Celastraceae	[39]
I63	3,16-dioxo-12α-hydroxyfriedelane	*Maytenus gonoclada* Martius	Celastraceae	[40]
I64	25-hydroxyfriedelane-3,21-dione	*Siphonodon celastrineus*	Celastraceae	[41]
I65	25-benzoyloxyfriedelane-3,21-dione	*Siphonodon celastrineus*	Celastraceae	[41]
I66	7β-hydroxy-3-oxo-D:A-friedooleanan-28-oic acid	*Celastrus vulcanicola*	Celastraceae	[42]
I67	7β-hydroxy-3-oxo-D:A-friedooleanan-28-oic acid methyl ester	*Celastrus vulcanicola*	Celastraceae	[42]
I68	7β,29-dihydroxy-3-oxo-D:A-friedooleanane	*Celastrus vulcanicola*	Celastraceae	[42]
I69	1β,30-dihydroxy-3-oxo-D:A-friedooleanane	*Celastrus vulcanicola*	Celastraceae	[42]
I70	1β-hydroxy-3-oxo-D:A-friedooleanan-30-oic acid	*Celastrus vulcanicola*	Celastraceae	[42]

续表1

I71	3-oxo-D:A-friedooleanan-28,30-olide	*Maytenus jelskii*	Celastraceae	[42]
I72	3α-hydroxy-D:A-friedooleanan-28-oic acid	*Maytenus jelskii*	Celastraceae	[42]
I73	3,12-dioxofriedelan-28-al	*Celastrus monospermus* Roxb.	Celastraceae	[43,44]
I74	3-oxo-11β-hydroxyfriedelane	*Celastrus monospermus* Roxb.	Celastraceae	[43,44]
I75	3,12-dioxo-28-hydroxyfriedelane	*Celastrus monospermus* Roxb.	Celastraceae	[43,44]
I76	3-oxo-12α,28-dihydroxyfriedelane	*Celastrus monospermus* Roxb.	Celastraceae	[43,44]
I77	3,16-dioxo-29-hydroxyfriedelane	*Maytenus robusta*	Celastraceae	[45]
I78	3-oxo-16β,29-dihydroxyfriedelane	*Maytenus robusta*	Celastraceae	[45]
I79	1,3-dioxofriedelan-26-al	*Salacia prinoides* DC	Hippocrateaceae	[46]
I80	3-oxo-26-hydroxyfriedelane	*Salacia prinoides* DC	Hippocrateaceae	[46]
I81	3-oxo-friedelan-26-al	*Salacia prinoides* DC	Hippocrateaceae	[46]
I82	1,3-dioxo-24-hydroxyfriedelane	*Salacia prinoides* DC	Hippocrateaceae	[46]
I83	1,3-dioxofriedelan-24-oic acid	*Salacia prinoides* DC	Hippocrateaceae	[46]
I84	3-oxo-21α,26-dihydroxyfriedelane	*Salacia reticulata* Var.	Hippocrateaceae	[47-49]
I85	3-oxo-21α,30-dihydroxyfriedelane	*Salacia reticulata* Var. Diandra	Hippocrateaceae	[47-49]
I86	3-oxofriedelan-30-al	*Salacia reticulata* Var. Diandra	Hippocrateaceae	[47-49]
I87	3-oxofriedelan-30-oic acid	*Salacia reticulata* Var. Diandra	Hippocrateaceae	[47-49]
I88	3-oxo-21β,26-dihydroxy-friedelane	*Salacia reticulata* Var. Diandra	Hippocrateaceae	[49]
I89	3,21-di-oxo-26- hydroxyfriedelane	*Salacia reticulata* Var. Diandra	Hippocrateaceae	[49]
I90	3-oxo-6β,26-dihydroxyfriedelane	*Salacia reticulata* Var. Diandra	Hippocrateaceae	[49]
I91	3-oxo-26-hydroxyfriedelane	*Salacia reticulata* Var. Diandra	Hippocrateaceae	[49]
I92	3,21-dioxo-6β,27-dihydroxyfriedelane	*Salacia reticulata* Var. Diandra	Hippocrateaceae	[49]
I93	3,15-dioxo-26-hydroxyfriedelane	*Salacia chinensis*	Hippocrateaceae	[50,51]
I94	3,15-dioxo-7α-hydroxyfriedelane	*Salacia chinensis*	Hippocrateaceae	[50,51]
I95	3-oxo-15α,29-dihydroxyfriedelane	*Salacia chinensis*	Hippocrateaceae	[50,51]
I96	3-oxo-15α,26-dihydroxyfriedelane	*Salacia chinensis*	Hippocrateaceae	[50,51]
I97	3-oxo-7α,26-dihydroxyfriedelane	*Salacia chinensis*	Hippocrateaceae	[50,51]
I98	3-oxo-15α-hydroxyfriedelane	*Salacia chinensis*	Hippocrateaceae	[50,51]
I99	3-oxo-2α-hydroxyfriedelan-29-oic acid	*Salacia chinensis*	Hippocrateaceae	[50,51]
I100	29-hydroxyfriedelan-3-on-28-al		Hippocrateaceae	[52]
I101	3-oxo-16α-hydroxyfriedelane	*Salacia elliptica*	Hippocrateaceae	[53]
I102	3-oxo-16α,28-dihydroxy-friedelane	*Salacia elliptica*	Hippocrateaceae	[53]
I103	3-oxo-16-methylfriedel-16-ene	*Salacia elliptica*	Hippocrateaceae	[53]
I104	30-hydroxy-D:A-friedoolean-1-en-3-one	*Salacia hainanensis* Chun et How	Hippocrateaceae	[54]
I105	21α-hydroxyfriedel-1-ene-3-one	*Salacia hainanensis* Chun et How	Hippocrateaceae	[55]
I106	friedelan-3β,30-diol diacetate	*Euphorbia antiquorum*	Euphorbiaceae	[56]
I107	30-acetoxy-friedelan-3β-ol	*Euphorbia antiquorum*	Euphorbiaceae	[56]
I108	3β-acetoxyfriedelan-30-ol	*Euphorbia antiquorum*	Euphorbiaceae	[56]
I109	3,7-dioxofriedelane	*Drypetes molunduana* and *Drypetes armoracia*	Euphorbiaceae	[57,58]
I110	3,15-dioxo-12α-hydroxy-3,15-dioxo-12α-hydroxy-friedelane	*Drypetes paxii* Hutch	Euphorbiaceae	[59]
I111	friedelan-3β-ol-25-al	*Drypetes paxii* Hutch	Euphorbiaceae	[59]
I112	7-oxofriedelane	*Drypetes paxii* Hutch	Euphorbiaceae	[59]
I113	3β-hydroxyfriedelane-7,12,22-trione	*Drypetes laciniata* Hutch.	Euphorbiaceae	[60]
I114	3α-(*E*)-*p*-coumaroyloxyfriedelan-7-one	*Drypetes hoaensis*	Euphorbiaceae	[61]
I115	3α-(*E*)-caffeoyloxyfriedelan-7-one	*Drypetes hoaensis*	Euphorbiaceae	[61]
I116	3-O-benzoylpluricostatic acid	*Trigonostemon xyphophylloides*	Euphorbiaceae	[62]

续表1

I117	3α-hydroxyfriedelan-25-al	*Drypetes inaequalis*	Euphorbiaceae	[63]
I118	friedelane-3α,16β-diol	*Drypetes congestiflora*	Euphorbiaceae	[64]
I119	3-oxo-2α-hydroxyfriedelane	*Quercus suber*	Fagaceae	[65]
I120	3-hydroxy-friedel-3-en-2-one	*Quercus suber*	Fagaceae	[65]
I121	3-oxo-28-hydroxyfriedelane	*Quercus suber*	Fagaceae	[65]
I122	2-oxo-3α-hydroxyfriedelane	*Quercus suber*	Fagaceae	[65]
I123	3-oxo-2β-acetoxyfriedelane	*Quercus suber*	Fagaceae	[65]
I124	2α,3β-dihydroxyfriedelan-28-oic acid	*Marila pluricostata*	Clusiaceae	[66]
I125	3-oxofriedelan-28-oic acid	*Marila pluricostata*	Clusiaceae	[66]
I126	3,28-dihydroxyfriedel-3-en-2-one	*Garcinia ovalifolia*	Clusiaceae	[67]
I127	3α,28-dihydroxyfriedelan-2-one	*Garcinia ovalifolia*	Clusiaceae	[67]
I128	3-oxofriedelane-27-al	*Caloncoba glauca*	Achariaceae	[68]
I129	3-oxofriedelan-27-oic acid	*Caloncoba glauca*	Achariaceae	[68]
I130	3-oxo-2α,29-dihydroxyfriedelane	*Lepidobotrys staudtii*	Lepidobotryaceae	[69]
I131	3-oxo-2β,21α-dihydroxyfriedelane	*Lepidobotrys staudtii*	Lepidobotryaceae	[69]
I132	3-oxo-6β,21α-dihydroxyfriedelane	*Lepidobotrys staudtii*	Lepidobotryaceae	[69]
I133	3-oxofriedelan-28-al	*Calophyllum inophyllum*	Calophyllaceae	[70]
I134	3β-hydroxyfriedelan-28-oic acid	*Calophyllum inophyllum*	Calophyllaceae	[70]
I135	27-hydroxyacetate canophyllic acid	*Calophyllum inophyllum*	Calophyllaceae	[70]
I136	3-oxo-27-hydroxyacetatefriedelan-28-oic acid	*Calophyllum inophyllum*	Calophyllaceae	[70]
I137	3-oxo-28-hydroxyfriedelan-27-oic acid	*Hibiscus tiliaceus*	Rhizophoraceae	[71]
I138	3-oxo-4α-hydroxyfriedelane	*Hibiscus tiliaceus*	Rhizophoraceae	[71]
I139	2α,3-dihydroxyfriedelane	*Hibiscus tiliaceus*	Rhizophoraceae	[71]
I140	3-oxo-2β-hydroxyfriedelan-29-oic acid	*Dichapetalum barteri*	Dichapetalaceae	[72]
I141	friedelan-3α-ol	*Dichapetalum barteri*	Dichapetalaceae	[72]
I142	3β-hydroxyfriedelan-17β-carboxylic acid	unidentified	unidentified	[73]
I143	friedelan-3,21α-diol	*Balanops australiana*	Balanopaceae	[74]
I144	friedelan-3α,28,29-triol	*Balanops australiana*	Balanopaceae	[74]
I145	friedelan14-ene-3α,28-diol	*Tamarix aphylla*	Tamaricaceae	[75]
I146	friedelan-14-ene-3β,28-diol	*Tamarix aphylla*	Tamaricaceae	[75]
I147	3-ketone-3-oxo-28-hydroxyfriedelan-14-en	*Tamarix aphylla*	Tamaricaceae	[75]
I148	4-epifriedelin	*Syzygium formosanum*	Myrtaceae	[76]

IIN1	17β-hydroxy-28-norfriedelan-3-one	*Elaeodendron glaucum*	Celastraceae	[11]
N2	17β,25-dihydroxy-28-norfriedelan-3-one	*Elaeodendron glaucum*	Celastraceae	[11]
N3	3-oxo-17-perhydroxy-28-nor-friedelane	*Maytenus diversifolia*	Celastraceae	[17]
N4	2,3,7-trihydroxy-6-oxo-1,3,5(10),7-tetraene-24-norfriedelane-29-oic acid methylester	*Crossopetalum gaumeri*	Celastraceae	[77]
N5	20-hydroxy-20-epitingenone	*Maytenus acanthophylla* Reissek	Celastraceae	[78]
N6	3-methyl-23-hydroxy-6-oxo-tingenol	*Tripterygium wilfordii* var. *regelii*	Celastraceae	[79,80]
N7	3-methyl-22β,23-dihydroxy-6-oxo-tingenol	*Tripterygium wilfordii* var. *regelii*	Celastraceae	[79,80]
N8	24,29-dinor-D:A- friedoolean-4-en-2β,22β-dihydroxy-3,21-dione	*Tripterygium wilfordii* var. *regelii*	Celastraceae	[79,80]
N9	22β-hydroxy-3,24,29-trinor-D:A-friedooleane-1(10),5,7-triene-4,21-dione-2-oic acid methyl ester	*Tripterygium wilfordii* Var. *regelii*	Celastraceae	[81]
N10	2β,22β-dihydroxy-3,21-dioxo-24-carboxyl-29-norfriedelan methyl ester	*Tripterygium wilfordii* Hook f.	Celastraceae	[82]
N11	2,3-dihydroxy-1,3,5(10),7-tetraene-6β(1'-hydroxyethyl)-24-norfriedelan-29-oic acid	*Tripterygium wilfordii* Hook f.	Celastraceae	[82]
N12	2,3-dihydroxy-1,3,5(10),7-tetraene-6α(1'-hydroxyethyl)-24-norfriedelan-29-oic acid	*Tripterygium wilfordii* Hook f.	Celastraceae	[82]
N13	regeol	*Tripterygium wilfordii* Hook f.	Celastraceae	[82]
N14	2,3-dihydroxy-24-norfriedelan-1,3,5(10)-triene-29-oic acid	*Tripterygium wilfordii* Hook f.	Celastraceae	[82]
N15	3β,22β-dihy-droxy-29-nor-D:A-friedoolean-21-one-2β,24-lactone	*Tripterygium wilfordii* Hook fil.	Celastraceae	[83,84]
N16	24,29-dinor-D:A-friedoolean-4-en-2β,6α,22β-trihydroxy-3,21-dione	*Tripterygium wilfordii* Hook fil.	Celastraceae	[83,84]
N17	2,3,22β-trihydroxy-21-oxo-24,29-dinor-D:A-friedoolean-1,3,5(10)-triene	*Tripterygium wilfordii* Var. *regelii*	Celastraceae	[85]
N18	2α,6β-dihydroxy-3-oxo-24-nor-D:A-friedoolean-4-ene-29-oic acid	*Tripterygium wilfordii* Var. *regelii*	Celastraceae	[85]

续表1

N19	2,3,7-trihydroxy-6-oxo-24-nor-D:A-friedoolean-1,3,5(10),7-tetraene	*Tripterygium wilfordii* Var. *regelii*	Celastraceae	[85]
N20	2β-hydroxy-3-oxo-24-norfriedelan-4-ene-29-oic acid	*Tripterygium wilfordii* Hook f.	Celastraceae	[86]
N21	2,23-dihydroxy-3-methoxy-6-oxo-1,3,5(10),7-tetraene-24-norfriedelane-29-oic acid	*Tripterygium hypoglaucum*	Celastraceae	[87]
N22	2-hydroxy-3-methoxy-6-oxo-1,3,5(10),7-tetraene-24-norfriedelane-29-oic acid	*Tripterygium hypoglaucum*	Celastraceae	[87]
N23	2,3-dihydroxy-3-methoxy-1,3,5(10),7-tetraene-24-norfriedelane-29-oic acid	*Tripterygium hypoglaucum*	Celastraceae	[87]
N24	2,3-dihydroxy-6-oxo-1,3,5(10),7-tetraene-24-norfriedelan-29-oic acid	*Tripterygium hypoglaucum*	Celastraceae	[88]
N25	25(9→8)-abeo-2,3-dihydroxy-1,3,5(10),6,8-pentaene-24-norfriedelan-29-oic acid	*Tripterygium hypoglaucum*	Celastraceae	[88]
N26	demethylzeylasteral	*Tripterygium hypoglaucum*	Celastraceae	[88]
N27	23-nor-6-oxodemethylpristimerol	*Tripterygium hypoglaucum*	Celastraceae	[88]
N28	demethylzeylasterone	*Tripterygium hypoglaucum*	Celastraceae	[88]
N29	25(9→8)Abeo-24-nor-friedelan-2,3-dioxo-1(10),4,6,9(11)-tetraen-29-oic acid	*Celastrus orbiculatus*	Celastraceae	[89]
N30	25(9→7)Abeo-24-nor-friedelan-2,3-dihydroxy-1,3,5(10),6,8,11-hexaen-29-oic acid	*Celastrus orbiculatus*	Celastraceae	[89]
N31	25(9→8)Abeo-24-nor-8,14-seco-friedelan-2,3-dihydroxy-1,3,5(10),6,8,14(27)-hexaen-29-oic acid	*Celastrus orbiculatus*	Celastraceae	[89]
N32	25(9→8),26(13→14)Abeo-24-nor-8,14-seco-friedelan-2,3-dihydroxy-1,3,5(10),6,8-pentaen-29(13)-olide	*Celastrus orbiculatus*	Celastraceae	[89]
N33	24-nor-friedelan-6α,10-dihydroxy-2,3-dioxo-4,7-dien-29-oic acid	*Celastrus stylosus*	Celastraceae	[90]
N34	celastrol	*Celastrus orbiculatus*	Celastraceae	[89]
N35	wilforol B	*Celastrus orbiculatus*	Celastraceae	[89]
N36	celastrol	*Reissantia buchananii*	Celastraceae	[91]
N37	tingenone	*Salacia chinensis*	Hippocrateaceae	[50,51]
N38	22β-hydroxytingen-one	*Salacia chinensis*	Hippocrateaceae	[50,51]
N39	regeol A	*Salacia chinensis*	Hippocrateaceae	[50,51]
N40	triptocalline A	*Salacia chinensis*	Hippocrateaceae	[50,51]
N41	salaquinone A	*Salacia chinensis*	Hippocrateaceae	[50,51]
N42	salaquinone B	*Salacia chinensis*	Hippocrateaceae	[50,51]
N43	salacin	*Salacia campestris*	Hippocrateaceae	[92]
N44	pristimerin	*Salacia campestris*	Hippocrateaceae	[92]
N45	20α-hydroxy-maytenin	*Salacia campestris*	Hippocrateaceae	[92]
N46	netzahualcoyene	*Salacia campestris*	Hippocrateaceae	[92]
N47	23-norfriedel-3-one	*Drypetes hainanensis*	Euphorbiaceae	[93]
N48	4-hydroxy-23-nor-friedel-3-one	*Drypetes hainanensis*	Euphorbiaceae	[94]
N49	3β,21α-dihydroxy-27-oxo-30-nor-(D:A)-friedo-oleane-27,20α-lactone	*Caloncoba glauca*	Achariaceae	[95]
N50	3,27-dioxo-30-nor-friedelan-20(29)-en-27,15α-lactone	*Caloncoba glauca*	Achariaceae	[96]
N51	3,27-dioxo-21β-hydroxy-30-norfriedelan-20(29)-en-27,15α-lactone	*Caloncoba glauca*	Achariaceae	[96]
N52	3β, 21β-dihydroxy-30-norfriedelan-27-oic acid	*Caloncoba glauca*	Achariaceae	[96]
N53	3β,24-diacetoxy-6β,7α,13α,18β-tetra-hydroxy-27,30-dinorfriedela-20(29)-en-22α-carboxylate	*Galphimia glauca*	Malpighiaceae	[97]
[III]**S1**	2,3-seco-2,3-epoxy-25-hydroxy-2,3-friedelanedione	*Crossopetalum lobatum* Lundell	Celastraceae	[25]
S2	2-hydroxy-3,4-secofriedelan-3-oic acid	*Crossopetalum lobatum* Lundell	Celastraceae	[30]
S3	methyl 2-oxo-3,4- secofriedelan-3-oate	*Crossopetalum lobatum* Lundell	Celastraceae	[30]
S4	methyl 2-hydroxy-3,4-secofriedelan-3-oate	*Crossopetalum lobatum* Lundell	Celastraceae	[30]
S5	3,4-secofriedelan-2,3-diol	*Crossopetalum lobatum* Lundell	Celastraceae	[30]
S6	4-oxo-friedo-3-nor-2,3-secoolean-2,29-dioic acid	*Crossopetalum lobatum* Lundell	Celastraceae	[84]
S7	2,3-seco-friedelan-2,24-olide-29-oic acid	*Tripterygium hypoglaucum*	Celastraceae	[68]

续表1

S8	2,3-seco-2,24-epoxy-3,24-olide-D:A-friedooleanane	*Cassine xylocarpa* and *Celastrus vulcanicola*	Celastraceae	[98]
S9	4-oxo-D:A-friedo-3-nor-2,3-secooleanane-2,29-dioic acid	*Tripterygium wilfordii* Hook fil.	Celastraceae	[99]
S10	violaic A	*Viola diffusa* Ging	Violaceae	[100]
S11	violaic B	*Viola diffusa* Ging	Violaceae	[100]
S12	violalide	*Viola diffusa* Ging	Violaceae	[100]
S13	(4R)-7α,24-diacetoxy-13α-carbomethoxy-1β,2β-epoxy-18β-hydroxy-30-nor-3,4-secofriedela-20(29)-en-3,4-olide	*Galphimia glauca*	Malpighiaceae	[97]
S14	(4R)-7α,22β,24-triacetoxy-13α-carbomethoxy-1β,2β-epoxy-18β-hydroxy-30-nor-3,4-secofriedela-20(29)-en-3,4-olide	*Galphimia glauca*	Malpighiaceae	[97]
S15	(4R)-7α,22β,12α,24-tetraacetoxy-13α-carbomethoxy-1β,2β-epoxy-18β-hydroxy-30-nor-3,4-secofriedela-20(29)-en-3,4-olide	*Galphimia glauca*	Malpighiaceae	[97]
S16	29-nor-3,4-seco-friedelan-4(23),20(30)-dien-3-oic acid	*Phyllanthus oxyphyllus*	Phyllanthaceae	[101]
S17	seco-3,4-friedelin	*Alchornea latifolia*	Euphorbiaceae	[102]
S18	24-nor-3,4-seco-friedelan-14(15)-en-3-oic acid	*Alchornea latifolia*	Euphorbiaceae	[102]
S19	3,4-secofriedelan-3,28-dioic acid	*Calophyllum inphyllum*	Clusiaceae	[70]
S20	3,4-seco-friedelan-3-oic acid	*Marila pluricostata*	Calophyllaceae	[66]
Ⅳ**E1**	D:B-friedoolean-3-ol-5,6-epoxy-29-oic acid	*Tripterygium wilfordii* var. *regelii*	Celastraceae	[80]
E2	epoxyfriedelan-2α-ol-24α-ethoxy-3β,24-epoxy-29-oic acid	*Tripterygium wilfordii* Hook fil.	Celastraceae	[99]
E3	3β,24-epoxy-2-oxo-3α-ol-friedelan-29-oic acid	*Tripterygium wilfordii* Hook f.	Celastraceae	[103]
E4	3β,24-Epoxy-2α,3α-dihydroxy-D:A-friedooleanan-29-oic acid methyl ester	*Maytenus jelskii*	Celastraceae	[42]
E5	2α-Acetoxy-3β,24-epoxy-3α-hydroxy-D:A-friedooleanan-29-oic acid methyl ester	*Maytenus jelskii*	Celastraceae	[42]
E6	1,3-dioxo-25,26-epoxyfriedelane	*Salacia prinoides* D.C.	Hippocrateaceae	[46]
E7	friedelan-3β,24-epoxy-3α-ol-29-oic acid	*Salacia chinesis* Linn. (*S. prinoides* DC.)	Hippocrateaceae	[51]
E8	friedelan-3β,24-epoxy-2α,3α-diol-29-oic acid	*Salacia chinesis* Linn. (*S. prinoides* DC.)	Hippocrateaceae	[51]
E9	1,3-dioxo-7,24-epoxyfriedelane	*Salacia oblonga*	Hippocrateaceae	[104]
E10	3-oxofriedelan-26→12β-lactone	*Gynocardia odorata*	Achariaceae	[105]
E11	3α-O-acetyl-friedelan-26→12β-lactone	*Gynocardia odorata*	Achariaceae	[105]
E12	3α-hydroxyfriedelan- 26→12β-lactone	*Gynocardia odorata*	Achariaceae	[105]
E13	3β,23-epoxy-friedelan-28-oic acid	*Calophyllum inophyllum* Linn	Calophyllaceae	[106]
Ⅴ**D1**	isoxuxuarines Aα	*Maytenus chuchuhuasca* (xuxua)	Celastraceae	[107]
D2	isoxuxuarines Aβ	*Maytenus chuchuhuasca* (xuxua)	Celastraceae	[107]
D3	7,8-dihydroisoxuxuarine Aα	*Maytenus chuchuhuasca* (xuxua)	Celastraceae	[107]
D4	7,8-dihydroxuxuarine Aα	*Maytenus chuchuhuasca* (xuxua)	Celastraceae	[107]
D5	xuxuarine Eβ	*Maytenus chuchuhuasca* (xuxua)	Celastraceae	[107]
D6	cangorosin A	*Maytenus ilicifolia* Mart	Celastraceae	[108]
D7	atropcangorosin A	*Maytenus ilicifolia* Mart	Celastraceae	[108]
D8	dihydroatropcangorosin A	*Maytenus ilicifolia* Mart	Celastraceae	[108]
D9	cangorosin B	*Maytenus ilicifolia* Mart	Celastraceae	[108]
D10	Celastroline Aα	*Celastrus orbiculatus*	Celastraceae	[89]
D11	Celastroline Aβ	*Celastrus orbiculatus*	Celastraceae	[89]
D12	Isocelastroline Aα	*Celastrus orbiculatus*	Celastraceae	[89]

注：Ⅰ–Intact friedelanes; Ⅱ–Norfriedelanes; Ⅲ–Secofriedelanes; Ⅳ–Epoxyfriedelanes; Ⅴ–Dimers。

2 木栓烷型三萜的NMR特征

2.1 木栓烷型三萜的^{13}C-NMR特征

木栓烷型三萜苷元中除了与氧相连的碳外，其余碳一般在δ60以下。在^{13}C-NMR中，角甲基一般出现在δ6.2~35.5，其中23-CH_3一般在6.2~13.5左右；23位为甲基时，24甲基的δ值为13.7~23.5；25–28位CH_3的δ值一般出现在18~32；29–30位甲基δ值一般为31~35。无氧取代时，-CH_2-的δ值一般分布于δ18–42左右，-CH-在δ37–60，而季碳的δ值则一般在δ33–57。木栓烷型三萜苷元和糖上与氧相连的碳δ值在60~90之间，具体而言，OH碳位δ61~82左右，乙酰基取代比

相应的OH取代向低场位移2~3左右。当有单OH或多OH取代时，会因为取代基效应而引起α-C向低场位移34~50，β-C向低场位移2~10左右，γ-C效应与前面两种效应相反，向高场位移0~9。烯碳为δ109~160左右，羰基碳δ170~220，一般羰基碳在δ180左右，而形成酯键则稍向高场位移，醛基碳则一般在δ195~210左右。以下综述了具有典型代表性的五类木栓烷型三萜的^{13}C-NMR数据。

2.1.1 基本结构木栓烷型三萜的^{13}C-NMR特征

正常结构的木栓烷型三萜的^{13}C-NMR特征一般与上述相似，在角甲基无氧取代的情况下一般会出现8个角甲基信号，最具特征的是23-CH_3一般在δ6.2~13.5左右，当23-CH_3为β型时，δ值一般在10以下；当23-CH_3为α型时，由于空间效应的影响，其与24-CH_3中的H的斥力作用减弱导致直接相连C的电子云密度减弱，从而减小了屏蔽效应，化学位移移向低场，一般出现在δ13.5附近。当相应位置出现氧代时由于氧的吸电子效应会使相应的C的δ值升高。见表2。

2.1.2 降碳木栓烷型三萜的^{13}C-NMR特征

降碳木栓烷型三萜一般降碳的位置出现在取代甲基部位：如23-nor（N47和N48）、24-nor（N8和N29-N33）、29-nor（N8）、30-nor（N49）等。此类三萜^{13}C-NMR最大特征就是甲基信号的相应减少。见表3。

2.1.3 开环木栓烷型三萜的^{13}C-NMR特征

该种类型的木栓烷型三萜最典型的结构特征是母环中A环的开环，且最常见的开环位置一般为3,4-seco（如S2-S5、S10-S20）或2,3-seco（如S1、S6-S9）。在开环部位一般都有-O-原子的介入，使得相应开环部位的化学位移向低场移动。另外，在开环的同时也常常伴随着降碳现象的出现（S9、S16）。见表4。

2.1.4 环氧木栓烷型三萜的^{13}C-NMR特征

该类型的三萜在结构上保留了木栓烷母环的完整性，其结构特点是在母环外接有环外的环氧桥，这使得环氧桥上与-O-原子相连的-C-原子化学位移向低场移动。见表5。

2.1.5 二聚体类木栓烷型三萜的^{13}C-NMR特征

该类三萜的结构特征是由2分子的木栓烷母环聚合而成，一般为一边含有1个醌环（quinoid），具有典型的醌类化合物碳信号；另一边带有一个芳香环（aromatic），具有芳香化合物碳信号。通常各相应位置的碳信号为成对出现的。见表6。

表2 正常结构木栓烷型三萜的^{13}C-NMR数据

C	I1	I22	I62	I63	I64	I113	I121	I125	I133	I134
1	22.3	15.8	202.7	22.3	24.6	17.0	22.2	22.2	22.2	16.6
2	41.5	35.2	60.6	41.2	42.5	35.7	41.5	41.5	41.5	35.5
3	213.3	72.7	204.1	212.3	212.8	70.4	213.2	213.2	213.0	71.4
4	58.2	49.1	59.1	58.0	58.5	49.1	58.2	58.2	58.2	50.0
5	42.1	37.1	37.8	41.8	42.4	42.2	42.1	42.0	42.0	38.4
6	41.3	41.7	40.6	40.8	41.7	58.1	41.2	41.5	41.0	42.2
7	18.2	17.5	18.1	18.4	18.0	209.9	18.0	18.1	18.0	17.9
8	53.1	53.2	50.6	52.0	53.9	63.8	52.4	53.0	52.8	53.6
9	37.4	37.8	37.3	38.1	42.0	44.2	37.4	37.8	37.1	38.3
10	59.4	61.3	71.9	59.1	60.7	60.6	59.4	59.2	59.2	61.8
11	35.6	35.5	34.2	47.3	30.0	52.0	35.4	35.9	35.4	36.4
12	30.5	30.6	29.8	71.2	31.4	212.0	30.0	31.0	30.6	31.7
13	39.7	39.7	38.8	45.7	39.9	55.1	39.3	38.9	38.7	39.3
14	38.3	38.3	38.7	40.8	37.9	48.4	38.1	38.9	37.6	38.5
15	32.4	32.3	30.5	50.3	33.0	32.2	31.3	32.6	32.4	33.3
16	36.0	36.1	35.9	218.3	35.0	37.4	29.0	34.8	34.9	30.4
17	30.0	30.0	32.5	45.5	33.1	43.1	35.1	44.7	47.7	45.1
18	42.8	42.8	44.2	45.4	41.9	35.6	39.4	37.8	36.4	37.7
19	35.3	35.3	36.0	38.5	37.0	34.3	34.4	35.4	35.4	36.6
20	28.1	28.2	34.3	27.8	42.7	32.9	28.1	28.4	28.3	28.9
21	32.7	32.8	74.3	31.5	218.7	54.5	31.3	32.4	32.4	33.3
22	39.2	39.3	47.0	30.7	55.0	217.3	33.3	29.4	28.0	36.0
23	6.8	11.6	7.3	6.8	7.0	12.2	6.8	6.8	6.8	12.6
24	14.6	16.4	16.0	14.6	14.7	17.4	14.6	14.6	14.6	17.0
25	17.9	18.2	18.2	18.7	62.7	20.0	18.0	17.5	17.2	18.2
26	20.2	18.6	17.8	20.5	20.9	21.4	19.0	20.6	20.0	20.9
27	18.6	20.1	19.3	9.0	18.4	18.5	19.2	18.5	18.8	18.9
28	32.1	31.8	33.1	27.3	33.6	28.3	68.0	183.3	209.1	179.4
29	35.0	35.0	24.9	31.3	28.8	24.3	34.2	34.5	34.5	34.9
30	31.8	32.1	31.8	35.0	25.0	32.8	32.8	29.7	29.4	30.5

续表2

C	I65	I66	I67	I104	I105	I116	I117	I118	I126	I127
1	24.8	22.4	22.4	149.0	130.2	23.9	21.0	19.6	32.3	36.1
2	42.6	41.7	41.7	130.1	148.9	67.7	37.0	36.6	194.9	211.8
3	212.3	212.7	212.7	201.9	201.9	78.4	71.2	72.2	142.5	76.8
4	58.6	58.8	58.8	57.7	57.7	42.7	53.3	53.1	140.7	54.5
5	42.3	41.3	41.3	43.7	43.6	37.5	38.3	38.2	39.5	38.0
6	41.6	48.9	48.9	39.9	39.8	40.9	41.9	41.3	38.3	40.5
7	18.2	68.3	68.3	17.4	17.7	17.5	18.0	18.1	17.9	17.5
8	54.0	52.9	52.6	52.2	50.7	53.0	52.2	53.2	52.0	52.5
9	41.1	37.6	37.6	36.6	36.6	37.8	51.5	37.1	36.7	37.6
10	60.3	59.8	59.8	62.2	62.2	51.5	58.2	60.1	55.6	60.3
11	30.1	31.1	31.2	34.6	36.0	35.1	28.2	35.9	34.5	34.5
12	30.7	37.8	37.5	30.2	30.2	31.1	31.2	31.9	29.0	31.2
13	39.9	39.5	39.5	39.9	39.1	36.7	39.2	40.1	39.3	38.1
14	37.9	44.6	44.9	38.3	38.8	38.9	38.2	39.2	39.4	38.0
15	33.1	32.8	32.8	31.9	29.9	32.6	31.4	44.2	31.1	31.3
16	34.9	29.2	29.1	35.8	36.0	29.6	35.7	75.6	31.2	29.9
17	33.0	38.4	38.3	30.0	32.5	44.7	30.0	37.7	35.1	35.1
18	41.8	38.4	38.0	42.7	44.3	37.8	42.8	44.7	39.4	39.4
19	36.9	35.1	35.1	29.3	34.3	34.8	35.5	35.6	34.4	34.4
20	42.7	28.5	28.5	33.4	36.0	28.4	28.1	28.0	28.1	28.1
21	218.7	35.8	35.9	28.1	74.2	32.6	32.8	35.6	33.3	31.2
22	55.0	32.4	32.5	38.1	47.0	36.0	38.9	30.8	29.8	33.3
23	7.0	6.9	6.9	6.7	6.7	10.7	10.6	9.9	10.3	10.8
24	14.8	16.1	16.1	13.7	13.7	15.7	14.7	14.6	17.8	14.2
25	65.1	18.8	18.8	19.9	17.4	17.6	204.7	18.3	18.8	17.6
26	21.5	21.7	21.4	19.5	20.1	20.3	19.6	21.3	19.0	19.0
27	18.6	18.5	18.5	18.6	19.2	18.5	18.5	20.3	18.8	19.1
28	33.8	183.3	179.2	32.1	33.1	182.0	31.9	24.9	68.0	68.0
29	28.8	34.3	34.4	28.9	24.9	34.5	35.1	35.4	34.2	34.3
30	25.0	29.7	29.6	71.9	31.8	29.7	31.6	30.7	32.8	31.2
OCOPh	166.8	-	-	-	-	166.9	-	-	-	-
ipso	130.2	-	-	-	-	130.1	-	-	-	-
ortho	129.5	-	-	-	-	129.6	-	-	-	-
metha	128.6	-	-	-	-	128.5	-	-	-	-
Para	133.1	-	-	-	-	133.1	-	-	-	-

C	I68	I69	I70	I71	I72	I73	I74	I75	I76	I77	I78
1	22.3	74.0	74.0	27.6	19.3	22.3	25.0	22.3	22.3	22.17	22.22
2	41.7	30.1	29.7	41.2	36.3	41.1	41.6	41.1	41.3	41.34	41.43
3	212.8	213.2	213.2	213.0	71.9	212.1	213.3	212.0	212.8	212.20	212.78
4	58.8	53.3	53.3	57.9	52.9	58.0	58.1	58.1	58.2	57.91	58.04
5	41.3	42.7	42.7	41.7	37.4	42.1	43.1	42.2	41.9	41.96	42.14
6	49.0	41.2	41.2	40.7	40.9	40.7	42.2	40.9	41.1	40.82	41.11
7	68.4	18.2	18.1	17.8	17.4	18.3	17.9	18.6	18.2	18.54	18.41
8	52.9	53.0	53.1	51.5	52.6	53.2	52.8	52.2	52.1	52.32	53.32
9	37.2	36.9	36.9	37.4	37.0	43.8	44.1	44.4	38.4	37.51	37.42
10	60.0	52.4	52.4	59.0	59.6	58.9	60.1	59.3	59.4	58.99	59.31
11	37.6	35.9	32.7	34.8	35.6	51.3	76.9	51.2	47.2	35.24	35.61
12	30.5	30.5	29.5	30.4	30.9	213.1	42.0	214.3	73.0	28.95	30.74
13	40.4	39.8	39.7	37.5	37.8	54.1	41.1	55.6	44.8	38.96	40.06
14	39.1	38.4	38.0	38.4	38.6	42.4	38.2	44.0	40.5	40.59	39.11
15	32.4	32.1	30.2	32.6	32.3	32.1	32.4	30.0	37.5	50.17	44.28
16	35.8	35.4	35.3	29.3	29.2	27.2	35.9	29.3	32.1	218.38	74.40
17	30.5	30.0	30.0	42.4	44.5	47.2	30.0	34.5	36.0	45.68	36.45
18	41.6	42.7	42.4	38.5	37.6	30.3	42.5	33.1	40.3	43.24	44.09
19	29.6	28.9	31.3	34.1	34.5	35.8	35.4	33.7	31.7	30.14	30.36
20	33.1	33.4	40.2	32.8	28.2	28.7	28.1	28.3	28.3	32.68	33.14
21	27.9	28.2	28.2	31.0	35.1	32.8	32.7	36.1	33.4	27.04	27.51
22	39.4	28.1	38.2	22.0	32.2	34.0	39.2	31.0	29.3	31.14	36.45
23	6.9	6.9	6.8	6.6	9.6	6.9	6.9	6.9	6.8	6.87	6.88
24	16.1	14.3	14.3	14.3	14.3	14.5	14.8	14.6	14.6	14.56	14.60
25	19.0	17.9	17.5	17.0	17.4	17.6	12.9	18.4	19.5	17.25	18.06
26	21.8	20.0	20.9	19.0	20.3	20.1	20.1	18.1	19.2	20.27	20.08
27	18.3	18.7	17.7	16.1	18.3	19.0	19.5	19.7	12.2	15.93	21.43
28	32.1	32.2	32.0	177.0	183.7	209.5	32.0	68.5	67.8	27.44	25.44
29	74.5	28.9	31.8	26.7	29.5	34.0	31.7	33.3	34.0	74.06	74.45
30	26.0	72.0	183.1	79.7	34.2	29.1	35.0	33.6	32.9	25.84	25.71

表3 降碳木栓烷型三萜的^{13}C-NMR数据

C	N8	N29	N30	N31	N32	N33	N47	N48	N49
1	28.1	121.3 d	106.2 d	104.5	104.6	37.7	21.9	22.0	16.7
2	71.5	182.0 s	146.9 s	147.5	144.7	194.4	41.5	38.2	35.7
3	200.1	182.2 s	144.4 s	144.2	144.2	199.4	212.0	211.2	72.8
4	127.7	131.4 s	128.7 s	118.1	118.0	123.1	59.9	84.8	50.2
5	159.2	142.1 s	117.6 s	129.8	129.8	154.3	39.2	44.7	38.5
6	30.9	121.3 d	121.6 d	122.6	122.5	74.5	43.4	39.9	42.4
7	20.8	153.2 d	130.0 s	127.9	127.9	122.6	18.1	17.8	18.4
8	47.7	47.6 s	141.7 s	131.3	131.3	153.9	53.5	53.2	49.6
9	37.6	144.8 s	132.2 s	135.3	135.6	51.5	37.1	37.2	37.3
10	52.3	158.2 s	131.8 s	129.5	129.5	71.3	57.3	55.8	61.7
11	33.1	128.3 d	129.0 d	29.3	25.5	29.6	35.4	35.6	36.4
12	29.5	38.9 t	138.1 d	35.9	32.8	28.7	30.4	30.4	28.2
13	39.5	41.6 s	44.1 s	35.9	102.5	38.4	39.7	39.7	49.9
14	40.0	43.2 s	49.0 s	156.8	43.6	41.9	38.3	38.3	40.7
15	28.1	24.8 t	31.3 t	34.1	38.8	28.4	32.4	32.5	28.6
16	29.7	38.6 t	38.8 t	41.4	40.2	36.0	36.0	35.9	37.1
17	44.9	33.2 s	32.4 s	41.6	42.6	30.7	30.0	30.0	32.5
18	45.3	48.2 d	43.2 d	50.4	46.0	43.7	42.7	42.8	42.9
19	31.7	32.6 t	32.7 t	36.8	32.8	30.6	35.3	35.3	23.7
20	41.3	41.7 s	41.9 s	41.9	40.2	40.6	28.2	28.1	84.5
21	214.0	31.1 t	31.0 t	30.8	36.8	29.9	32.7	32.7	73.1
22	77.2	34.5 t	36.2 t	35.5	36.9	35.0	39.2	39.2	37.8
23	11.2	11.2 q	11.6 q	11.6	11.6	9.2	-	-	12.0
24	-	-	-	-	-	-	20.6	13.2	16.7
25	15.6	27.7 q	19.5 q	20.7	20.5	27.0	17.6	17.9	18.9
26	19.1	20.5 q	20.1 q	28.0	23.2	21.2	20.3	20.3	15.6
27	17.5	20.5 q	23.4 q	108.3	23.2	18.6	18.7	18.7	78.8
28	25.2	31.8 q	31.7 q	31.3	25.1	31.8	32.1	32.1	31.9
29	-	183.2 s	183.6 s	184.7	180.5	186.2	35.0	35.0	25.0
30	14.8	34.0 q	32.5 q	25.9	26.3	32.4	31.7	31.7	-

表4 开环木栓烷型三萜的^{13}C-NMR数据

C	S1	S2	S3	S4	S5	S8	S9	S10	S11	S12	S16
1	27.8	31.6	35.1	32.3	27.3	98.9	32.7	29.5	29.3	29.4	21.2
2	170.4	72.4	194.3	72.5	73.4	143.2	176.4	69.3	68.0	69.1	37.1
3	177.0	179.5	162.3	162.3	65.7	178.1	-	177.0	175.4	176.9	179.2
4	47.3	36.3	36.3	36.3	36.3	40.1	213.8	84.9	82.3	84.5	150.9
5	38.9	39.6	38.2	38.4	38.4	43.3	54.0	40.2	39.9	40.0	42.0
6	34.5	39.1	38.7	39.1	39.2	28.2	37.4	37.8	37.4	36.9	41.4
7	17.1	18.3	18.2	18.3	18.2	17.3	18.1	18.3	17.7	19.7	17.7
8	52.0	52.9	52.7	53.0	52.9	47.7	50.7	52.6	52.3	47.7	49.5
9	35.3	37.0	37.0	37.2	37.1	38.8	38.7	38.2	37.5	37.3	38.7
10	46.1	55.4	52.7	55.9	55.9	47.8	50.2	60.4	59.7	59.3	58.4
11	32.0	35.4	35.9	35.4	35.5	33.9	34.4	37.9	37.4	35.2	34.9
12	30.1	30.2	30.2	30.0	30.1	28.7	29.5	27.7	27.2	22.5	28.8
13	39.6	38.4	38.4	38.9	38.7	38.9	39.8	54.5	52.8	50.5	40.6
14	38.0	39.6	39.7	39.7	39.9	37.6	39.6	39.1	38.5	48.3	39.5
15	32.3	32.4	32.3	32.4	32.4	28.8	29.8	33.0	31.8	80.5	28.3
16	35.7	36.2	36.1	36.2	36.2	35.9	36.7	35.6	28.1	40.0	36.1
17	30.0	30.0	30.0	30.0	30.3	30.1	30.5	30.7	35.3	30.8	31.3
18	42.6	43.0	43.0	43.0	43.0	44.2	44.8	43.2	38.7	43.9	45.4
19	35.2	35.4	35.3	35.3	35.3	30.2	31.1	36.1	34.5	28.4	29.8
20	28.1	28.2	28.1	28.2	29.7	40.3	40.8	28.4	28.4	33.2	149.3
21	32.6	33.0	32.9	32.9	33.0	29.9	30.6	32.3	30.2	28.0	30.8
22	39.1	39.3	39.2	39.3	39.3	36.2	37.5	38.5	32.8	34.4	38.2
23	12.5	7.4	7.0	7.4	7.5	7.9	25.6	16.2	16.0	16.2	111.0
24	20.6	19.3	20.1	19.3	19.1	99.4	18.0	13.5	13.1	13.2	18.1
25	72.6	17.9	18.1	17.8	17.9	17.5	18.7	18.4	18.5	16.3	19.3
26	20.2	20.2	20.1	20.2	20.1	15.9	18.3	22.7	21.2	13.6	15.1
27	18.5	18.8	18.6	18.8	18.6	17.2	16.8	181.6	177.5	179.9	18.1
28	32.1	31.9	31.9	31.8	31.8	31.6	32.2	30.9	65.5	29.1	31.4
29	35.0	34.9	34.9	34.9	34.9	179.0	181.3	30.3	31.6	25.1	-
30	31.6	32.2	32.1	32.2	32.1	31.8	32.1	35.5	34.6	74.3	107.3
OMe	-	-	-	-	-	51.3	-	-	-	-	-
CO_2Me	-	-	50.7	52.2	-	-	-	-	-	-	-

表5　环氧木栓烷型三萜的^{13}C-NMR数据

C	E1	E2	E3	E4	E5	E13
1	18.3	28.0	34.2	26.7 t	25.9 t	16.6
2	30.3	69.2	207.4	73.2 d	75.4 d	18.8
3	76.0	85.4	103.1	106.8 s	105.6 s	66.5
4	39.1	44.7	51.2	45.7 d	47.4 d	58.0
5	64.9	50.4	47.5	47.0 s	46.8 s	38.3
6	52.2	30.1	33.3	33.6 t	33.3 t	42.4
7	21.9	19.7	19.1	19.2 t	19.2 t	18.0
8	45.1	51.0	50.3	49.7 d	49.8 d	53.5
9	35.1	37.8	37.8	37.0 s	37.1 s	37.8
10	49.3	53.6	57.2	52.6 d	53.2 d	61.8
11	35.3	37.0	34.1	34.1 t	34.3 t	36.0
12	29.4	30.3	29.0	29.0 t	29.0 t	31.7
13	39.6	39.7	39.2	39.1 s	39.2 s	39.3
14	39.3	39.9	39.0	49.1 s	39.1 s	38.3
15	29.3	29.8	29.5	29.0 t	29.1 t	33.3
16	36.8	34.9	36.0	36.2 t	36.2 t	30.5
17	30.6	30.8	30.1	30.1 s	30.1 s	45.1
18	45.0	45.1	44.0	44.5 d	44.5 d	38.4
19	30.7	31.2	30.3	30.4 t	30.4 t	35.4
20	40.7	41.1	40.4	40.5 s	40.6 s	28.9
21	30.5	30.8	29.4	30.0 t	30.0 t	33.3
22	36.9	37.9	36.7	36.4 t	36.6 t	36.4
23	25.4	15.2	7.2	6.9 q	7.1 q	59.3
24	20.9	104.0	72.7	72.2 t	72.4 t	18.8
25	18.3	17.4	16.8	16.7 q	16.7 q	18.2
26	15.9	18.4	16.7	16.1 q	16.2 q	20.9
27	17.8	17.2	17.9	17.4 q	17.5 q	18.8
28	31.9	32.5	31.8	31.8 q	31.9 q	181.5
29	32.8	181.8	184.4	179.1 s	179.4 s	34.9
30	182.7	32.6	31.4	32.0 q	32.1 q	30.4
31 (CH_2)	-	64.2	-	-	-	-
32 (Me)	-	16.1	-	-	-	-

表6　二聚体类木栓烷型三萜的^{13}C-NMR数据

C	D1	D2	D3	D4
1 (1’)	115.9 d (110.4 d)	115.2 d (110.7 d)	113.1 d (110.4 d)	112.6 d (111.4 d)
2 (2’)	190.3 s (144.5 s)	189.6 s (144.3 s)	191.4 s (144.5 s)	191.4 s (144.6 s)
3 (3’)	91.9 s (138.4 s)	90.7 s (138.5 s)	91.3 s (138.3 s)	91.5 s (137.7 s)
4 (4’)	79.4 s (129.5 s)	77.1 s (128.4 s)	79.5 s (129.4 s)	79.5 s (127.8 s)
5 (5’)	130.7 s (123.2 s)	132.4 s (124.0 s)	134.3 s (123.3 s)	133.6 s (124.6 s)
6 (6’)	125.9 d (187.2 s)	128.4 d (187.6 s)	133.7 d (187.0 s)	134.4 d (187.7 s)
7(7’)	116.1 d (126.1 d)	116.9 d (126.1 d)	24.1 t (126.2 d)	24.3 t (126.2 d)
8 (8’)	160.3 s (170.4 s)	163.6 s (170.4 s)	41.1 d (170.1 s)	41.5 d (170.7 s)
9 (9’)	41.4 s (39.9 s)	43.9 s (39.8 s)	37.3 s (39.9 s)	37.5 s (39.8 s)
10 (10’)	173.0 s (151.8 s)	173.1 s (151.1 s)	169.6 s (151.8 s)	170.4 s (150.4 s)
11 (11’)	33.2 t (34.3 t)	33.1 t (34.3 t)	30.5 t (34.4 t)	30.5 t (34.4 t)
12 (12’)	29.7 t (30.1 t)	29.9 t (30.3 t)	29.3 t (30.1 t)	29.4 t (30.2 t)
13 (13’)	39.4 s (40.2 s)	39.9 s (40.2 s)	40.0 s (40.1 s)	40.1 s (40.2 s)
14 (14’)	44.2 s (44.3 s)	44.0 s (44.3 s)	40.2 s (44.3 s)	40.2 s (44.4 s)
15 (15’)	28.2 t (28.3 t)	28.5 t (28.4 t)	27.9 t (28.4 t)	28.0 t (28.4 t)
16 (16’)	35.4 t (35.4 t)	35.5 t (35.6 t)	35.3 t (35.5 t)	35.3 t (35.6 t)
17 (17’)	38.2 s (30.2 s)	38.2 s (38.2 s)	38.1 s (38.2 s)	38.1 s (38.2 s)
18 (18’)	43.4 d (43.3 d)	43.5 d (43.5 d)	43.8 d (43.4 d)	43.9 d (43.5 d)
19 (19’)	32.1 t (32.0 t)	31.9 t (32.0 t)	31.8 t (32.0 t)	31.8 t (32.0 t)
20 (20’)	41.8 d (41.9 d)	41.9 d (41.9 d)	42.2 d (41.9 d)	42.3 d (41.9 d)
21 (21’)	213.8 s (213.8 s)	213.7 s (213.6 s)	213.9 s (213.6 s)	213.9 s (213.6 s)
22 (22’)	52.3 t (52.6 t)	52.4 t (52.6 t)	53.4 t (52.6 t)	53.5 t (52.6 t)
23 (23’)	22.0 q (13.2 q)	24.2 q (12.8 q)	22.7 q (13.4 q)	22.8 q (13.0 q)
25 (25’)	35.5 q (38.6 q)	40.0 q (38.9 q)	22.8 q (38.7 q)	22.8 q (38.5 q)
26 (26’)	22.3 q (20.7 q)	22.4 q (20.9 q)	15.7 q (20.8 q)	15.7 q (20.8 q)
27 (27’)	19.8 q (20.0 q)	19.7 q (19.7 q)	18.1 q (19.8 q)	18.2 q (19.7 q)
28 (28’)	32.4 q (32.5 q)	32.5 q (32.6 q)	32.6 q (32.7 q)	32.7 q (32.6 q)
29 (29’)	-	-	-	-
30 (30’)	15.0 q (15.0 q)	15.14 q (15.14 q)	15.1 q (15.2 q)	15.2 q (15.1 q)

续表6

C	D5	D10	D11	D12
1 (1’)	114.7 d (110.6 d)	116.0 d (111.2 d)	114.8 d (110.8 d)	115.9 d (110.4 d)
2 (2’)	189.4 s (145.2 s)	187.8 s (144.4 s)	187.3 s (145.0 s)	190.8 s (144.7 s)
3 (3’)	91.0 s (137.5 s)	92.2 s (137.5 s)	90.8 s (137.4 s)	92.0 s (138.2 s)
4 (4’)	77.3 s (128.3 s)	79.1 s (127.2 s)	76.9 s (128.3s)	79.4 s (129.5 s)
5 (5’)	131.8 s (123.8 s)	130.3 s (124.4 s)	131.7 s (123.6 s)	130.5 s (123.0 s)
6 (6’)	128.8 d (187.4 s)	126.6 d (192.0 s)	128.8 d (189.9 s)	125.9 d (187.5 s)
7(7’)	117.2 d (126.1 d)	116.0 d (126.0 d)	117.3 d (126.1 d)	116.2 d (126.0 d)
8 (8’)	164.4 s (171.2 s)	161.8 s (171.4 s)	164.4 s (171.0 s)	161.2 s (171.4 s)
9 (9’)	43.9 s (40.0 s)	41.9 s (40.3 s)	43.8 s (40.0 s)	41.6 s (40.0 s)
10 (10’)	173.2 s (151.1 s)	174.4 s (150.1 s)	173.4 s (151.1 s)	173.4 s (151.9 s)
11 (11’)	32.8 t (34.0 t)	32.8 t (34.0 t)	32.9 t (33.8 t)	32.8 t (34.2 t)
12 (12’)	29.8 t (29.8 t)	29.2 t (29.3 t)	29.4 t (29.1 t)	29.2 t (29.9 t)
13 (13’)	38.6 s (39.0 s)	38.1 s (38.9 s)	38.9 s (38.5 s)	37.9 s (39.0 s)
14 (14’)	44.4 s (44.7 s)	44.6 s (44.7 s)	44.3 s (44.6 s)	44.6 s (44.6 s)
15 (15’)	28.6 t (28.5 t)	28.3 t (28.3 t)	28.6 t (28.4 t)	28.5 t (28.5 t)
16 (16’)	36.4 t (36.4 t)	36.3 t (36.2 t)	36.2 t (36.2 t)	36.3 t (36.3 t)
17 (17’)	30.5 s (30.5 s)	30.5 s (30.4 s)	30.4 s (30.3 s)	30.5 s (30.4 s)
18 (18’)	44.2 d (44.2 d)	44.0 d (44.1 d)	44.1 d (44.1 d)	44.2 d (44.0 d)
19 (19’)	30.9 t (30.8 t)	30.9 t (30.5 t)	30.6 t (30.7 t)	30.6, t (31.1 t)
20 (20’)	40.5 s (40.4 s)	40.0 s (39.7 s)	40.3 s (40.1 s)	40.3 s (40.2 s)
21 (21’)	29.8 t (29.5 t)	29.6 t (29.5 t)	29.8 t (29.7 t)	29.4 t (29.3 t)
22 (22’)	35.0 t (34.7 t)	34.6 t (34.4 t)	34.8 t (34.5 t)	34.7 t (34.4 t)
23 (23’)	24.6 q (13.2 q)	22.2 q (12.9 q)	24.5 q (13.2 q)	22.4 q (13.2 q)
25 (25’)	39.2 q (37.7 q)	34.8 q (36.8 q)	39.2 q (37.5 q)	37.5 q (34.7 q)
26 (26’)	22.3 q (20.9 q)	22.4 q (20.7 q)	22.5 q (20.9 q)	22.0 q (20.9 q)
27 (27’)	18.2 q (18.4 q)	18.8 q (18.6 q)	18.5 q (18.8 q)	18.9 q (18.8 q)
28 (28’)	31.6 q (31.5 q)	31.6 q (31.3 q)	31.5 q (31.5 q)	31.6 q (31.5 q)
29 (29’)	179.1 s (178.8 s)	184.5 s (183.6 s)	184.3 s (184.3 s)	184.4 s (183.6 s)
30 (30’)	32.9 q (32.7 q)	32.6 q (32.4 q)	32.4 q (32.2 q)	32.7 q (32.4 q)
COOMe	51.6 q (51.4 q)	-	-	-

2.2 木栓烷型三萜的^{1}H-NMR特征

在木栓烷型三萜氢谱中，主要包括甲基($-CH_3$)信号、亚甲基($-CH_2-$)信号、次甲基(-CH-)信号、双键质子(CH=CH)信号、以及常见的羟基(-OH)氢信号和羧基(-COOH)醛基(-CHO)等官能团的活泼氢信号。

在木栓烷型三萜中，$-CH_3$的氢化学位移在δ0.6-1.9之间，23-H一般以二重峰(d峰) 出现，一般在δ1.0左右；非取代基直接连接的$-CH_2-$一般在δ0.75-2.6之间，同一碳上的两个氢因空间位置不同，位移相差 δ0-0.9左右；非取代基直接相连的-CH-氢信号一般在δ0.67-2.75左右，4-H因与23-H相互偶合，一般以四重峰(q峰)出现。10和18-H则列分为2个二重峰(dd峰)。有OH等取代时，同碳H的δ值明显向低场移动。表7~11综述了具代表性的五类木栓烷型三萜的^{1}H-NMR数据特征。

表7 正常结构木栓烷型三萜的^{1}H-NMR数据 (mult, *J* in Hz)

H	I62	I113	I118
1	-	1.22 (m), 1.40 (m)	-
2	3.23 (1H, d, 15.8)	1.66 (m), 2.12 (m)	-
	3.44 (1H, d, 15.8)	-	-
3	-	3.94 (q-like, 2.0, Heq)	3.34 (dt, 10.0, 4.4)
4	2.55 (1H, q, 7.0)	1.55 (m)	-
5	-	-	-
6	1.39 (1H, m)	2.20 (d, 11.4, Heq)	-
	1.87 (1H, br dd, 9.5, 3.0)	2.45 (d, 11.4, Hax)	-
7	1.41 (1H, m), .52 (1H, m)	-	-
8	1.28 (1H, m)	3.55 (s)	-
9	-	-	-
10	2.37 (1H, s)	2.00 (m)	-
11	1.18 (1H, m)	2.30 (d, 11.4, Heq),	-
	2.14 (1H, ddd, 13.5, 7.0, 3.5)	2.90 (d, 11.4, Hax)	-

续表7

12	1.26 (1H, m), 34 (1H, m)	1.31 (m)	-
15	1.27 (1H, m), 44 (1H, m)	1.52 (m),1.70 (m),	-
16	1.53 (1H, m), .60 (1H, m)	2.00 (m)	4.00 (t, 8.8)
17	-	2.50 (m)	-
18	1.51 (1H, m)	1.20 (m)	-
19	1.53 (1H, m)	1.70 (m)	-
	1.60 (1H, dd, 13.8, 4.8)	-	-
20	-	1.85 (d, 8.6, Hax);	-
	-	2.70 (d, 8.6, Heq)	-
21	3.67 (1H, dd, 12.0, 4.5)	-	-
22	1.21 (1H, dd, 12.0, 4.5)	-	-
	1.68 (1H, dd, 12.5, 12.0)	-	-
23	1.03 (3H, d, 7.0)	1.05 (d, 6.6)	0.90 (d, 6.8)
24	0.67 (3H, s)	1.31 (s)	0.77 (s)
25	1.19 (3H, s)	0.99 (s)	0.82 (s)
26	0.92 (3H, s)	1.46 (s)	1.06 (s)
27	1.07 (3H, s)	1.44 (s)	0.96 (s)
28	1.18 (3H, s)	1.24 (s)	1.17 (s)
29	0.96 (3H, s)	1.27 (s)	0.96 (s)
30	1.05 (3H, s)	1.16 (s)	1.02 (s)

H	**I64**	**I77**	**I78**	**I126**
1	2.07 (m)	1.89 β, 1.62 α	1.59 β, 1.84 α	2.53 (1H, dd), 2.42 (1H, dd)
2	2.12 (m),2.23 (m)	2.28, 2.38	2.33 β, 2.23 α	-
3	2.37 (ddd, 13.3, 4.0, 1.8)	-	-	-
4	-	2.22 α	2.18 α	-
5	2.25 (m)	-	-	-
6	1.82 (m)	1.21 α, 1.70 β	1.16 α, 1.61 β	1.94 (1H, m), 1.46 (1H, m)
7	1.88 (m), .48 (m)	1.40 β, 1.30 α	1.36 β, 1.46 α	1.43 (1H, m), 1.56 (1H, m)
8	1.56 (m)	1.40 α	1.37 α	1.43 (1H, m)
9	-	-	-	-
10	1.65 (m)	1.50 α	1.43 α	1.83 (1H, m)
11	1.24 (m), 2.07 (m)	1.19 α; 1.46 β	1.37 α, 1.18 β	1.46 (2H, m)
12	1.40 (m), 1.53 (m)	1.38 α, β	1.25 β, 1.61 α	1.87 (2H, m)
13	-	-	-	-
14	-	-	-	-
15	1.37 (m), 1.60 (m)	2.09 α, 2.40 β	1.48 β, 1.86 α	1.41 (2H, m)
16	1.42 (m), 1.78 (m)	-	4.11 α (t, 8.8)	1.31 (2H, m)
17	-	-	-	-
18	1.82 (m)	2.14 β	1.78 β	1.29 (1H, m)
19	1.62 (m), 1.86 (m)	1.58 α, 1.30 β	1.63 β, 1.33 α	1.40 (2H, m)
20	-	-	-	-
21	1.82 (m)	1.36, 1.68	1.40 β, 1.65 α	1.33 (2H, m)
22	2.61(d, 12.8), 0.91 (d, 6.6)	1.52, 1.91	1.45 α, 1.76 β	1.87 (2H, m)
23	0.83 (s)	0.89 (d, 6.8)	0.88 (d, 6.6)	1.83 (3H, s)
24	3.90 (d, 11.7)	0.70 (s)	0.70 (s)	1.11 (3H, s)
25	3.98 (d, 11.7)	0,85 (s)	0.84 (s)	1.08 (3H, s)
26	1.078 (s)	1.18 (s)	1.11 (s)	0.95 (3H, s)
27	1.18 (s)	0.87 (s)	1.02 (s)	1.10 (3H, s)
28	1.15 (s)	1.33 (s)	1.32 (s)	3.64 (1H, d, 15.5)
	-	-	-	3.65 (1H, d, 15.5)
29	1.08 (s)	3.34 (m)	3.36 (m)	0.95 (3H, s)
30	1.17 (s)	1.13 (s)	1.13 (s)	0.99 (3H, s)

表8 降碳木栓烷型三萜的^{1}H-NMR数据 (mult, *J* in Hz)

H	N33	N47	N48	N49
1	2.78 (d, 18.5), 3.16 (d, 18.0)	1.65 (m), 1.974 (m)	1.67 (m), 1.97 (m)	1.35 (m), 1.56 (m)
2	-	2.26 (m), 2.38 (m)	2.33 (m), 2.51 (m)	1.51 (m), 1.83 (m)
3	-	-	-	3.67 (m)
4	-	1.97 (m), 2.16 (m)	3.76 (br.s)	1.21 (m)
5	-	-	-	-
6	5.72 (s)	1.34 (m), 1.58 (m)	1.39 (m), 1.95 (m)	1.02 (m), 1.69 (m)
7	5.43 (s)	1.39 (m), 1.46 (m)	1.39 (m), 1.50 (m)	1.31, 1.45 (m)
8	-	1.40 (m)	1.38 (m)	2.69 (dd, 11.0, 1.0)
9	-	-	-	-
10	-	1.45 (m)	1.50 (m)	0.98 (br. d, 11.6)
11	1.55-1.62 (m), 1.40-1.47 (m)	1.27 (m), 1.45 (m)	1.29 (m), 1.44 (m)	1.11 (m), 1.56
12	1.54-1.61 (m), 0.93-0.99 (m)	1.34 (2H, m)	1.34 (2H, m)	1.73 (m), 1.81 (m)
13	-	-	-	-
14	-	-	-	-
15	1.53 (dd, 6.0, 18.5)	1.31 (m), 1.50 (m)	1.31 (m), 1.52(m)	1.39 (m), 1.63 (m)
	1.91 (dd, 5.0, 13.0)	-	-	-
16	1.72-1.80 (m), 1.39-1.43 (m)	1.35 (m), 1.56 (m)	1.33 (m), 1.55 (m)	1.16 (m), 1.63 (m)
17	-	-	-	-
18	1.48 (br. d, 8.0)	1.55 (m)	1.55 (m)	1.86 (m)
19	2.40 (br. d, 15.5),	1.20 (m), 1.35 (m)	1.19 (m), 1.35 (m)	1.91 (br. d), 2.23 (dd)
	1.60-1.68 (m)	-	-	-
20	-	-	-	-
21	2.22 (br. d, 13.5), 1.33-1.42 (m)	1.27 (m), 1.44 (m)	1.26 (m), 1.46 (m)	3.59 (br d, 3.6)
22	2.69-2.77 (m), 1.08-1.16 (m)	0.94 (m), 1.48 (m)	0.93 (m), 1.48 (m)	1.24 (br d), 1.95 (dd)
23	1.76 (s)	-	-	0.90 (d, 5.6)
24	-	0.88 (s)	0.73 (s)	0.93 (s)
25	0.90 (s)	0.85 (s)	0.86 (s)	0.89 (s)
26	1.03 (s)	1.01 (s)	1.01 (s)	0.87 (s)
27	1.01 (s)	1.04 (s)	1.05 (s)	-
28	1.08 (s)	1.18 (s)	1.17 (s)	1.19
29	-	0.95 (s)	0.94 (s)	1.30 (s)
30	1.25 (s)	1.00 (s)	0.99 (s)	-

表9 开环木栓烷型三萜的^{1}H-NMR数据 (mult, *J* in Hz)

H	S1	S9	S10	S11	S12
1	2.39 (d, 18.9 H_α)	2.69 (m, 1 H)	2.02 (m), 1.62 (m)	1.72(m), 1.50 (m)	2.07 (m), 1.58 (m)
	2.63 (dd, 7.5, 18.9, H_β)	2.33 (m, 1 H)	-	-	-
2	-	-	4.34 (dd, 12.0, 2.0)	4.41 (dd, 12.0, 2.0)	4.29 (dd, 12.0, 2.0)
3	-	-	-	-	-
4	2.55 (q, 7.1)	-	4.23 (q, 6.5)	4.38 (q, 6.5)	4.17 q (6.5)
5	-	-	-	-	-
6	1.68-1.70 (m)	1.94 (m, 1 H)	1.52 (m), 1.14 (m)	1.16 (m), 0.98 (m)	1.56 (m), 1.11 (m)
	-	1.60 (m, 1 H)	-	-	-
7	1.52	1.53 (m, 1 H)	1.64 (m), 1.46 (m)	-	1.55 (m), 1.47 (m)
	-	1.38 (m, 1 H)	-	-	-
8	1.48-1.51 (m)	1.67 (m, 1 H)	1.79 (m)	1.53 (m)	1.24 (m)
9	-	-	-	-	-
10	1.66-1.69 (m)	2.87 (dd, 6.4, 1H)	1.24 (m)	1.17 (m)	1.25 (m)
11	1.84 (br. d, 12.8)	1.86 (m, 1 H)	1.70 (m), 1.41 (m)	-	1.76 (m), 1.19 (m)
	-	1.57 (m, 1 H)	-	-	-
12	1.41-1.44 (m)	1.73 (m, 2 H)	2.10(m), 1.49 (m)	2.02 (m), 1.99 (m)	2.10 (m), 1.24 (m)
13	-	-	-	-	-
14	-	-	-	-	-
15	1.27, 1.48	1.38 (m, 2 H)	1.95 (m), 1.52 (m)	2.01 (m), 1.30 (m)	4.34 (br s)
16	1.55-1.58 (m)	1.77 (m, 1 H)	1.73 (m), 1.26 (m)	1.38 (m), 1.08 (m)	1.82 (m), 1.77 (m)
	-	1.47 (m, 1 H)	-	-	-
17	-	-	-	-	-
18	1.52	1.66 (m, 1 H)	1.82 (m)	1.44 (m)	1.97 (m)
19	1.36-1.40 (m)	2.71 (m, 1 H)	1.73 (m), 1.22 (m)	1.74 (m), 1.24 (m)	1.47 (m), 1.06 (m)
	-	1.75 (m, 1 H)	-	-	-
20	-	-	-	-	-
21	1.27 , 1.48	2.61 (m, 1 H)	1.43 (m), 1.25 (m)	1.31 (m), 1.21 (m)	1.73 (m), 1.52 (m)
	-	1.57 (m, 1 H)	-	-	-

续表9

22	0.95-0.98 (m)	2.33 (m, 1 H)	1.42 (m), 0.87 (m)	1.32 (m), 1.08 (m)	1.93 (m), 1.06 (m)
	1.48-1.51 (m)	1.08 (m, 1 H)	-	-	-
23	1.09 (d, 7.1)	2.44 (s, 3 H)	1.23 d (6.5)	1.05 (d, 6.5)	1.22 (d, 6.5)
24	1.13 (s)	1.27 (s, 3 H)	0.87 (s)	0.72 (s)	0.88 (s)
25	4.59, 4.64 (2d, 7.6)	0.99 (s, 3 H)	0.87 (s)	0.79 (s)	0.83 (s)
26	0.91 (s)	1.32 (s, 3 H)	1.12 (s)s	0.96 (s)	0.99 (s)
27	1.06 (s)	0.95 (s, 3 H)	-	-	-
28	1.18 (s)	1.21 (s, 3 H)	1.21 (s)	3.47 dd (10.0, 4.0)	1.13 (s)
	-	-	-	3.27 dd (10.0, 4.0)	-
29	0.95 (s)	-	0.99 (s)	0.92 (s)	0.98 (s)
30	1.00 (s)	1.49 (s, 3 H)	0.93 (s)s	0.91 (s)	3.24 (br s)

表10　环氧木栓烷型三萜的^{1}H-NMR数据 (mult, *J* in Hz)

H	**E2**	**E4**	**E5**	**E13**
1	1.98 (m, 1 H), 1.88 (m, 1 H)	1.72 (m), 1.91 (dt, 4.9, 13.7)	1.69, 2.04	1.92 (1H, m), 1.53 (1H, m)
2	4.49 (m, 1 H)	3.89 (d, 4.4)	5.03 (d, 4.4)	1.35 (1H, m), 1.08 (1H, m)
3	4.34 (d, 4, 1 H)	-	-	4.81 (1H, br d, 2.1)
4	2.54 (m, 1 H)	2.07 (d, 7.2)	1.91 (d, 7.1)	1.49 (1H, m)
5	-	-	-	-
6	1.38 (m, 2 H)	1.37,1.68 m	1.52, 1.80 m	1.98 (1H, br d, 12.2)
	-	-	-	1.28 (1H, m)
7	1.56 (m, 2 H)	1.10, 1.47	1.12, 1.49	1.43 (2H, m)
8	1.50 (m, 1 H)	1.30	1.32	1.40 (1H, m)
9	-	-	-	-
10	1.86 (m, 1 H)	1.56	1.47	1.07 (1H, m)
11	1.82 (m, 1 H), 1.48 (m, 1 H)	0.99 (m), 2.03	1.23, 1.36	1.48 (1H, m), 1.22 (1H, m)
12	2.54 (m, 2 H)	1.25, 1.46	1.32 , 1.46	1.55 (1H, m), 1.43 (1H, m)
13	-	-	-	-
14	-	-	-	-
15	1.74 (m, 2 H)	1.24, 1.43	1.25, 1.32	1.31 (1H, m), 1.23 (1H, m)
16	1.38 (m, 2 H)	1.37, 1.69	1.40, 1.69	2.76 (1H, dd, 14.0, 9.8)
	-	-	-	1.80 (1H, m)
17	-	-	-	-
18	1.68 (m, 1 H)	1.53	1.54 m	2.87 (1H, dd, 12.4, 3.4)
19	2.73 (br.d, 15, 1 H);	1.57, 2.35 (d, 15.0)	1.56 dd (5.2, 14.9)	1.51 (1H, m); 1.31 (1H, m)
	1.88 (m, 1 H)	-	2.36 d (14.9)	-
20	-	-	-	-
21	2.62 (m, 1 H), 1.57 (m, 1 H)	1.35, 2.18 (m)	1.38, 2.19 m	1.69 (2H, m)
22	2.41 (td, 14.3, 1 H),	0.98 (m)	0.98 m, 2.04	2.24 (1H, d, 12.4);
	1.16 (m, 1 H)	2.02 (dt, 4.0, 13.9)	-	1.80 (1H, m)
23	1.33 (m, 3 H)	0.97 (d, 6.9)	0.98 (d, 7.1)	4.43 (1H, t, 10.0)
	-	-	-	4.19 (1H, dd, 10.0, 3.4)
24	5.34 (s, 1 H)	3.61 (d, 8.3)	3.67 (d, 8.3)	1.35 (3H, s)
	-	4.10 (d, 8.3)	4.12 (d, 8.3)	-
25	1.11 (s, 3 H)	0.96 (s)	0.97 (s)	0.89 (3H, s)
26	1.28 (s, 3 H)	0.84 (s)	0.86(s)	1.09 (3H, s)
27	0.99 (s, 3 H)	0.83 (s)	0.87 (s)	1.07 (3H, s)
28	1.23 (s, 3 H)	1.08 (s)	1.10 (s)	-
29	-	-	-	1.02 (3H, s)
30	1.52 (s, 3 H)	1.19 (s)	1.21 (s)	1.35 (3H, s)
31 (CH_2)	4.07 (m, 1 H), 3.65 (m, 1 H)	-	-	-
32 (Me)	1.33 (m, 3 H)	-	-	-

表11 二聚体类木栓烷型三萜的^{1}H-NMR数据 (mult, *J* in Hz)

H	D1	D2	D3	D4	D5
H-1	6.13 (d, 1.6)	6.14 (d, 1.7)	6.01 (s)	6.01 (s)	6.08 (d, 1.5)
H-6	6.28 (dd, 1.6, 6.5)	6.61 (dd, 1.7, 7.0)	6.30 (br s)	6.31 (br s)	6.52 (dd, 1.5,7.0)
H-7	5.92 (d, 6.5)	6.13 (d, 7.0)	2.05 (m)	2.18 (m)	6.08 (d, 7.0)
	-	-	2.19 (m)	2.24 (m)	-
H-19α	-	-	-	-	2.39 (d, 15.6)
H-20	2.48 (m)	2.49 (m)	2.50 (m)	2.52 (m)	-
H-22α	2.83 (d, 14.3)	2.89 (d, 14.3)	2.87 (d, 14.4)	2.87 (d, 14.0)	-
Me-23	1.59 (s)	1.58 (s)	1.49 (s)	1.51 (s)	1.58 (s)
Me-25	1.48 (s)	1.49 (s)	1.12 (s)	1.13 (s)	1.38 (s)
Me-26	1.26 (s)	1.29 (s)	1.04 (s)	1.06 (s)	1.17 (s)
Me-27	0.99 (s)	0.98 (s)	1.23 (s)	1.27 (s)	0.53 (s)
Me-28	0.97 (s)	0.99 (s)	0.95 (s)	0.99 (s)	1.06 (s)
Me-30	0.98 (d, 7.0)	1.00 (d, 7.0)	0.99 (d, 6.4)	1.00 (d, 6.7)	1.16 (s)
COOMe	-	-	-	-	3.59 (s)
H-1′	7.03 (s)	6.98 (s)	6.99 (s)	6.84 (s)	6.74 (s)
H-7′	6.25 (s)	6.25 (s)	6.26 (s)	6.29 (s)	6.21 (s)
H-19′α	-	-	-	-	2.39 (d, 15.6)
H-20′	2.51 (m)	2.49 (m)	2.50 (m)	2.49 (m)	-
H-22′α	2.92 (d, 14.4)	2.91 (d, 14.5)	2.91 (d, 14.4)	2.91 (d, 14.3)	-
Me-23′	2.50 (s)	2.45 (s)	2.55 (s)	2.73 (s)	2.73 (s)
Me-25′	1.61 (s)	1.62 (s)	1.61 (s)	1.58 (s)	1.48 (s)
Me-26′	1.39 (s)	1.37 (s)	1.39 (s)	1.37 (s)	1.26 (s)
Me-27′	1.07 (s)	1.00 (s)	1.06 (s)	1.00 (s)	0.55 (s)
Me-28′	1.02 (s)	1.12 (s)	1.02 (s)	1.01 (s)	1.09 (s)
Me-30′	0.99 (d, 6.2)	1.00 (d, 7.0)	0.99 (d, 6.4)	0.99 (d, 6.7)	1.17 (s)
COOMe	-	-	-	-	3.48 (s)

3 结论

木栓烷型三萜是五环三萜中具有潜在药用价值的一类,其中一些化合物表现出了良好的生物活性,例如雷公藤红素(celastrol, N36)、卫矛酮(tingenone, N37)、扁塑藤素(pristimerin, N44)、violaic A(S10)、violaic B(S11)、violalide(S12)等,尤其是最近发现的结构独特且生物活性好的醌甲基化物降碳类、开环类、环氧类木栓烷型三萜,引起了许多相关研究者的极大关注。本文主要总结了近几十年来天然来源的木栓烷型三萜的结构特征,对这些化合物的NMR数据特征进行了分类归纳,以期对木栓烷型三萜化合物的结构解析研究提供一定的参考。

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