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(73) 专利权人 中国科学院昆明植物研究所

地址 650201 云南省昆明市蓝黑路 132 号

(72) 发明人 黎胜红 李春环 骆世洪

(74) 专利代理机构 昆明协立知识产权代理事务

所(普通合伙) 53108

代理人 马晓青

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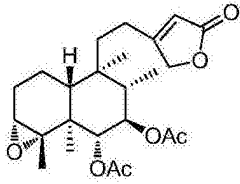
(54) 发明名称

克罗烷二萜化合物及其提取物和其作为昆虫拒食剂

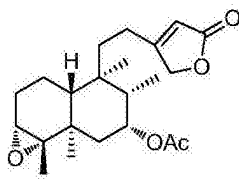
(57) 摘要

本发明提供藤状火把花提取物总二萜及活性化合物 1-27, 以其为活性成分的新型天然克罗烷二萜昆虫拒食剂, 其制备方法及其总二萜和活性化合物在制备昆虫拒食剂中的应用。本发明的昆虫拒食剂高效低毒, 使用安全, 无污染, 利于生态平衡, 且具有广谱性, 对多种植食性昆虫具有显著防治效果。

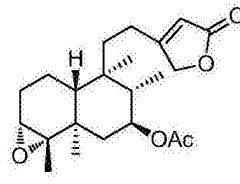
1. 下列结构式所示的二萜类化合物1-27,



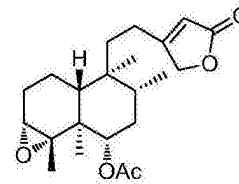
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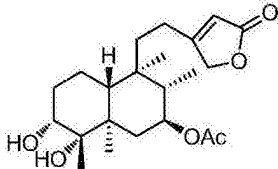
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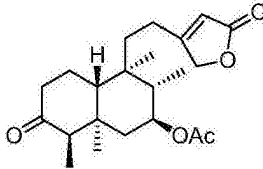
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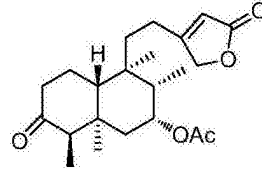
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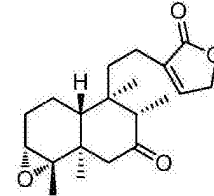
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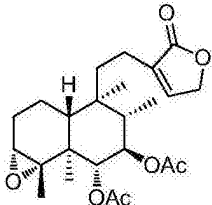
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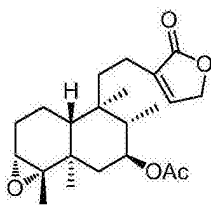
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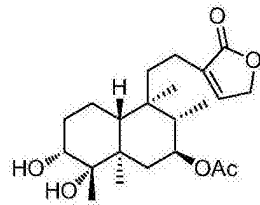
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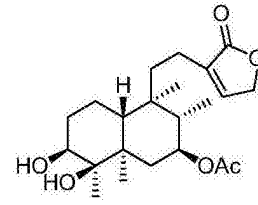
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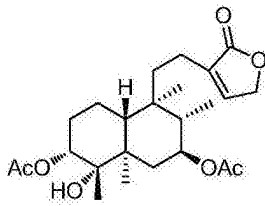
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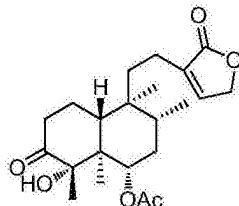
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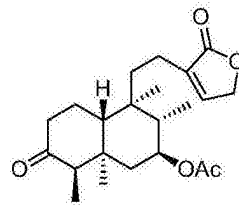
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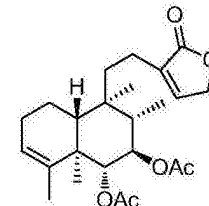
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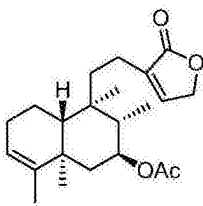
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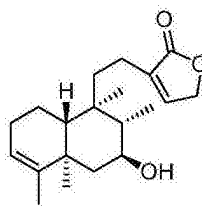
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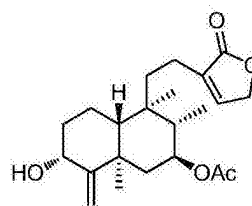
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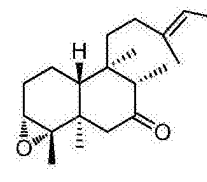
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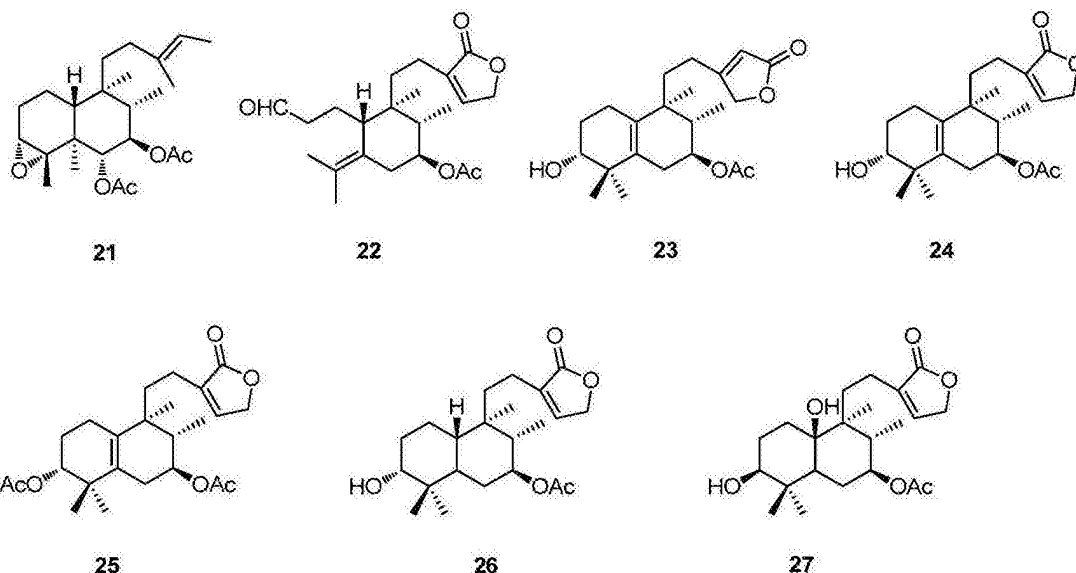
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2. 昆虫拒食剂,以权利要求1所述的任一化合物1-27或其组合为活性成分,添加拒食剂常规辅料制成制剂。

3. 藤状火把花提取物总二萜,其特征在于用有机溶剂甲醇或乙醇或氯仿或丙酮或乙醚或石油醚或正己烷或环己烷直接冷浸或者热回流提取新鲜藤状火把花地上部分或其干燥粗粉,或者先用上述有机溶剂冷浸或热回流提取新鲜藤状火把花地上部分或其干燥粗粉后再用乙酸乙酯或氯仿萃取得到提取物总二萜,所述提取物含有权利要求1中的二萜化合物1-27的一个或多个,化合物1-27总的含量以重量百分比计大于70%。

4. 昆虫拒食剂,其特征在于以权利要求3的藤状火把花提取物总二萜为活性成分,添加拒食剂常规辅料制成制剂。

5. 权利要求1所述的任一化合物1-27或其组合或权利要求3所述的藤状火把花提取物总二萜用作为昆虫拒食剂。

6. 权利要求1所述的任一化合物1-27或其组合或权利要求3所述的藤状火把花提取物总二萜在制备昆虫拒食剂中的应用。

7. 如权利要求6所述的应用,其特征在于总二萜是以0.5~200 $\mu\text{g}/\text{mL}$ 的量施用于基材上,单个化合物1-27或任意组合是按0.05~120 nM/cm^2 的量施用于基材上,与载体和/或媒体相结合。

8. 如权利要求6所述的应用,其特征在于所述昆虫拒食剂用于植物表面或其生长环境中。

9. 如权利要求6所述的应用,其特征在于所述昆虫拒食剂防治植食性昆虫棉铃虫、甜菜夜蛾、斜纹夜蛾、小菜蛾、玉米螟。

10. 权利要求1所述化合物1-27的制备方法,将藤状火把花植物叶或花或茎阴干,粉碎,用石油醚在室温下浸提3次,依次提取24h,36h和48h,提取液合并,减压浓缩提取液得石油醚浸膏;提取后剩下的植物残渣晾干,用甲醇在室温下浸提3次,依次提取24h,36h和48h,提取液回收溶剂后得到甲醇浸膏;甲醇浸膏加水稀释,用乙酸乙酯萃取3次,合并回收有机溶剂得到乙酸乙酯浸膏;将石油醚浸膏和乙酸乙酯浸膏合并得到总二萜部位;总二萜部位用适量氯仿/丙酮溶解后用200-300目硅胶拌样,进行硅胶柱层析,以1:0,1:1,0:1的石油醚-氯仿和1:0,9:1,8:2,7:3,1:1,0:1的氯仿-丙酮进行梯度洗脱,用TLC进行检测,合并相同流

份,依次得到八个部分:A-H;将C部分经多次乙醚,甲醇洗结晶,丙酮重结晶得化合物1,母液浓缩后以石油醚/乙酸乙酯,石油醚/丙酮为洗脱条件反复进行硅胶柱层析,同时结合Sephadex LH-20,1:1的氯仿/甲醇柱层析,得到化合物5,6,9,10,15,和19;将D部分,即氯仿/丙酮9/1部分的样品进行MCI柱层析,以甲醇-水60%,70%,80%,90%,100%梯度洗脱;70%部分有结晶析出,待洗结晶后得化合物3,从80%部分以丙酮洗结晶得化合物2;剩余部分分别经多次正相硅胶柱层析、Sephadex LH-20柱层析,氯仿/甲醇1:1和丙酮以及半制备HPLC得到化合物4,8,13,14,16,19,20,21,22,24和25;将E部分经多次乙醚,丙酮重结晶得到化合物11,洗液浓缩后反复用正相硅胶柱层析和Sephadex LH-20,氯仿/甲醇1:1和丙酮柱层析得到化合物7,12,17,18,23,26和27。

克罗烷二萜化合物及其提取物和其作为昆虫拒食剂

技术领域：

[0001] 本发明属于昆虫拒食剂领域，具体地，涉及藤状火把花提取物总二萜和克罗烷型二萜化合物1-27，以它们为活性成分的天然二萜昆虫拒食剂，其制备方法及其总二萜和活性化合物在制备昆虫拒食剂中的应用。

背景技术：

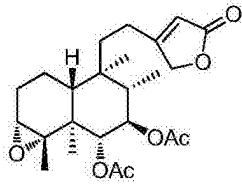
[0002] 当前主要采用化学农药防治农业病虫害，但随着时间的推移，农药残留、害虫的再猖獗与抗性等问题把化学农药的弊端逐渐暴露出来，促使人们开始寻找生态合理的有效控制害虫的新方法。从天然产物中筛选出安全高效的化合物，直接开发为新的生物农药或以其为模型合成新的更安全高效的农药是创新生物农药发展的主要方向。其中，植物源拒食剂由于其解决了传统农药的环境污染及害虫易产生抗性两大主要问题，因而受到科学界及产业界的重视，成为新型生物农药研究的一个重要分支。例如，对除虫菊、印楝以及鱼藤等杀虫植物的研究都很成功，开发了除虫菊酯、印楝素和鱼藤酮等著名农药，为防治一些世界性害虫做出了突出贡献。但这些杀虫植物的缺点是受栽培区域限制，因此生产成本较高。藤状火把花(*Colquhounia seguinii* var. *seguinii*)为唇形科(Lamiaceae)，火把花属(*Colquhounia*)植物。其为灌木，直立攀援，主要产于云南西北部至中部及东部，广西西部，贵州，四川，湖北西部，此外缅甸北部也有，植物资源非常丰富。目前，还未见关于藤状火把花植物化学成分的报道。

发明内容：

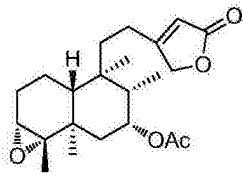
[0003] 本发明的目的是提供一类新型的藤状火把花提取物总二萜及活性化合物1-27，以其为活性成分的天然二萜拒食剂，它们的制备方法，进一步的目的是提供总二萜和活性化合物在制备昆虫拒食剂中的应用。

[0004] 本发明的下述技术方案是用来达到上述的发明目的：

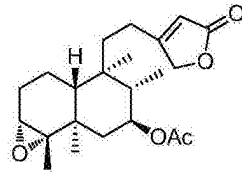
[0005] 下列结构式所示的二萜类化合物1-27，



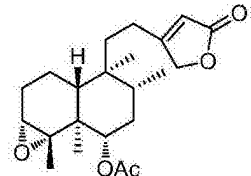
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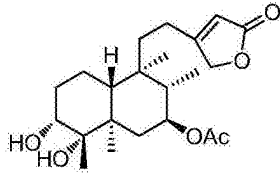
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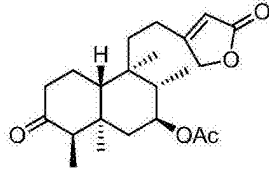
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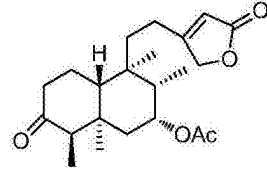
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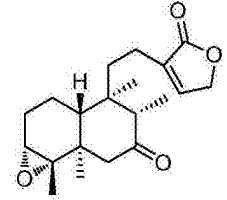
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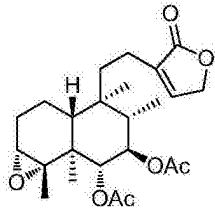


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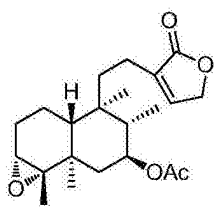


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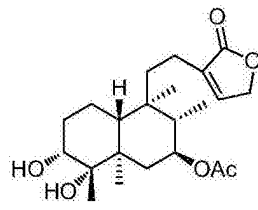
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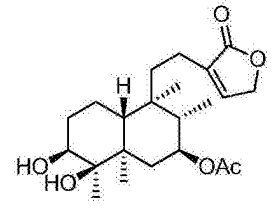
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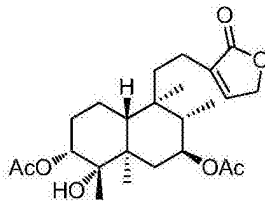
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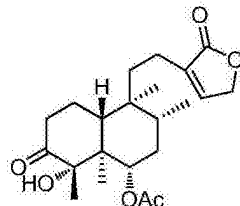
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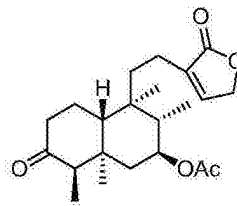
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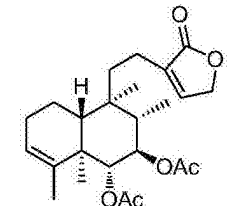
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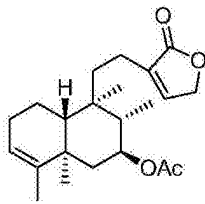
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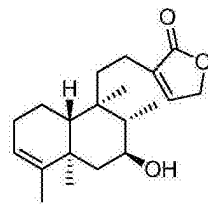
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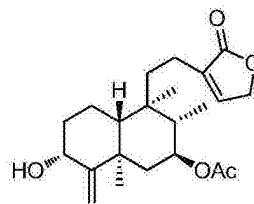
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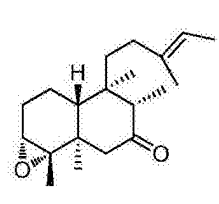
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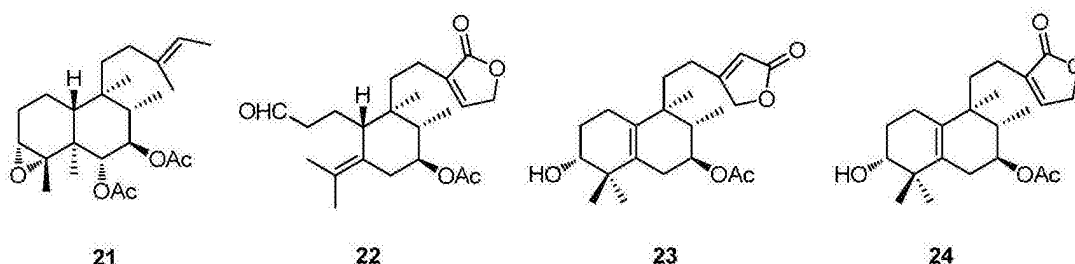
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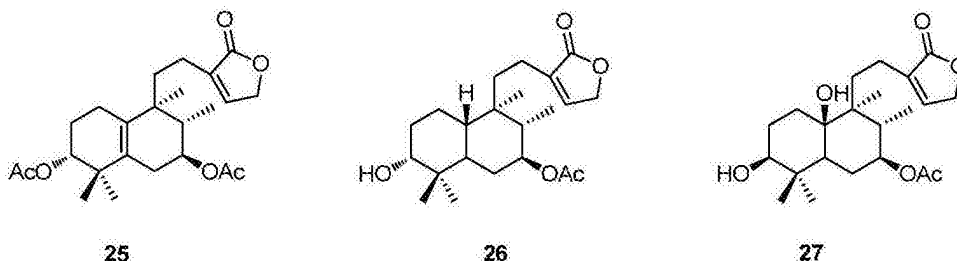
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[0007]



[0008] 昆虫拒食剂,以所述的任一化合物1-27或其组合为活性成分,添加拒食剂常规辅料制成制剂。

[0009] 藤状火把花提取物总二萜,用有机溶剂甲醇或乙醇或氯仿或丙酮或乙醚或石油醚或正己烷或环己烷直接冷浸或者热回流提取新鲜藤状火把花地上部分或其干燥粗粉,或者先用上述有机溶剂冷浸或热回流提取新鲜藤状火把花地上部分或其干燥粗粉后再用乙酸乙酯或氯仿萃取得到提取物总二萜,所述提取物含有上述二萜化合物1-27的一个或多个,化合物1-27总的含量以重量百分比计大于70%。

[0010] 昆虫拒食剂,以藤状火把花提取物总二萜为活性成分,添加拒食剂常规辅料制成制剂。

[0011] 所述的任一化合物1-27或其组合或所述的藤状火把花提取物总二萜用作为昆虫拒食剂。

[0012] 所述的任一化合物1-27或其组合或所述的藤状火把花提取物总二萜在制备昆虫拒食剂中的应用。

[0013] 所述化合物1-27的制备方法,将藤状火把花植物叶或花或茎阴干,粉碎,用石油醚在室温下浸提3次,依次提取24h,36h和48h,提取液合并,减压浓缩提取液得石油醚浸膏;提取后剩下的植物残渣晾干,用甲醇在室温下浸提3次,依次提取24h,36h和48h,提取液回收溶剂后得到甲醇浸膏;甲醇浸膏加水稀释,用乙酸乙酯萃取3次,合并回收有机溶剂得到乙酸乙酯浸膏;将石油醚浸膏和乙酸乙酯浸膏合并得到总二萜部位;总二萜部位用适量氯仿/丙酮溶解后用200-300目硅胶拌样,进行硅胶柱层析,以1:0,1:1,0:1的石油醚-氯仿和1:0,9:1,8:2,7:3,1:1,0:1的氯仿-丙酮进行梯度洗脱,用TLC进行检测,合并相同流份,依次得到八个部分:A-H;将C部分经多次乙醚,甲醇洗结晶,丙酮重结晶得化合物1,母液浓缩后以石油醚/乙酸乙酯,石油醚/丙酮为洗脱条件反复进行硅胶柱层析,同时结合Sephadex LH-20,1:1的氯仿/甲醇柱层析,得到化合物5,6,9,10,15,和19;将D部分,即氯仿/丙酮9/1部分的样品进行MCI柱层析,以甲醇-水60%,70%,80%,90%,100%梯度洗脱;70%部分有结晶析出,待洗结晶后得化合物3,从80%部分以丙酮洗结晶得化合物2;剩余部分分别经多次正相硅胶柱层析、Sephadex LH-20柱层析,氯仿/甲醇1:1和丙酮以及半制备HPLC得到化合物4,8,13,

14,16,19,20,21,22,24和25;将E部分经多次乙醚,丙酮重结晶得到化合物11,洗液浓缩后反复用正相硅胶柱层析和Sephadex LH-20,氯仿/甲醇1:1和丙酮柱层析得到化合物7,12,17,18,23,26和27。

[0014] 本发明的二萜拒食剂经活性测试显示具有很强的昆虫拒食活性。在实际应用中,本发明总二萜是以如下的量施用于基材或一种群上:所述量的范围为0.5~200 $\mu\text{g}/\text{mL}$,优选在1~40 $\mu\text{g}/\text{mL}$,与载体和/或媒体相结合;本发明二萜化合物是以单个化合物或不同化合物的任意组合物按如下的量施用于基材或一种群上:所述量的范围0.05~120 nM/cm^2 ,优选在0.05~50 nM/cm^2 ,与载体和/或媒体相结合。

[0015] 本发明的二萜拒食剂用于植物表面或其生长环境中,可防治棉铃虫、甜菜夜蛾、斜纹夜蛾、小菜蛾、玉米螟等多种植食性昆虫。

[0016] 本发明的二萜拒食剂可制成乳剂、水剂、水乳剂、可湿型粉剂,优选的形式是乳剂和水乳剂。

[0017] 本发明的昆虫拒食剂高效低毒,使用安全,无污染,利于生态平衡,且具有广谱性,对多种植食性昆虫具有显著防治效果。

[0018] 具体实施方法:

[0019] 下面的实施例可以使本专业人员更全面地理解本发明,但不以任何方式限制本发明。

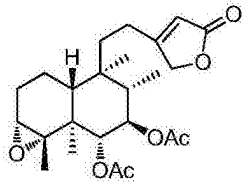
[0020] 实施例1:

[0021] 本发明提取物总二萜及克罗烷二萜化合物1-27的提取、分离和纯化:

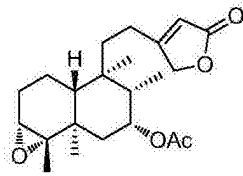
[0022] 将藤状火把花植物叶或花或茎阴干,粉碎到30目,用石油醚在室温下浸提3次,每次10L,依次提取24h,36h和48h,提取液合并,减压浓缩提取液得石油醚浸膏。提取后剩下的植物残渣晾干,用甲醇在室温下浸提3次,每次8L,依次提取24h,36h和48h,提取液回收溶剂后得到甲醇浸膏。甲醇浸膏加1L水稀释,用1L乙酸乙酯萃取3次,合并回收有机溶剂得到乙酸乙酯浸膏。将石油醚浸膏和乙酸乙酯浸膏合并得到总二萜部位。总二萜部位用适量氯仿/丙酮溶解后用200-300目硅胶拌样,进行硅胶柱层析,以石油醚-氯仿(0:1,1:1,0:1)和氯仿-丙酮(1:0,9:1,8:2,7:3,1:1,0:1)进行梯度洗脱,用TLC进行检测,合并相同流份,依次得到八个部分:A-H。将C部分经多次乙醚,甲醇洗结晶,丙酮重结晶得样品化合物1,母液浓缩后以石油醚/乙酸乙酯,石油醚/丙酮为洗脱条件反复进行硅胶柱层析,同时结合Sephadex LH-20(氯仿/甲醇,1:1)柱层析,得到化合物5,6,9,10,15,和19。将D部分,即氯仿/丙酮9/1部分的样品进行MCI柱层析,以甲醇-水(60%,70%,80%,90%,100%)梯度洗脱。70%部分有结晶析出,待洗结晶后得化合物3,而从80%部分以丙酮洗结晶得化合物2。剩余部分分别经多次正相硅胶柱层析、Sephadex LH-20柱层析(氯仿/甲醇1:1和丙酮)以及半制备HPLC得到化合物4,8,13,14,16,19,20,21,22,24和25。将E部分经多次乙醚,丙酮重结晶得到化合物11,洗液浓缩后反复用正相硅胶柱层析和Sephadex LH-20(氯仿/甲醇1:1和丙酮)柱层析得到化合物7,12,17,18,23,26和27。所述提取物总二萜部分含有二萜化合物1-27的一个或多个,应用高效液相色谱分析,化合物1-27总的含量以重量百分比计大于70%。

[0023] 实施例2:

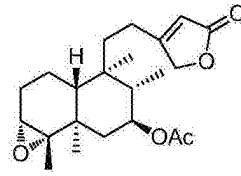
[0024] 本发明实施例1所得化合物1-27的结构式如下所示:



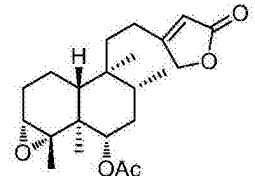
1



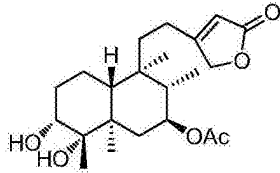
2



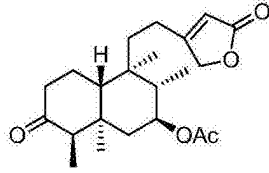
3



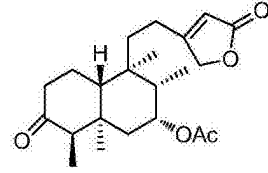
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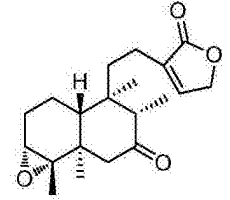
5



6

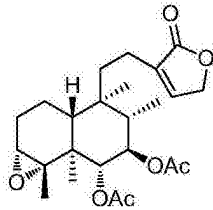


7

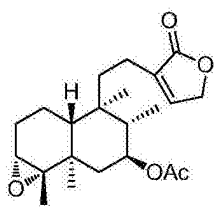


8

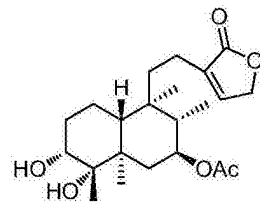
[0025]



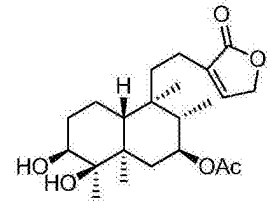
9



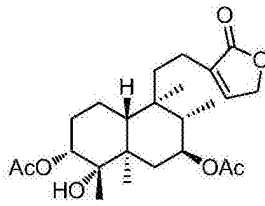
10



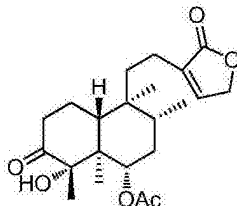
11



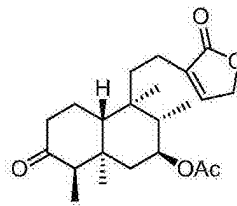
12



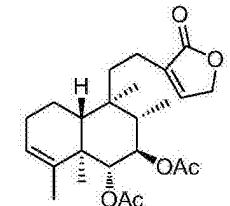
13



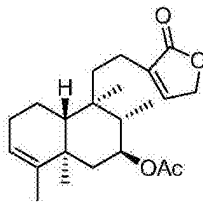
14



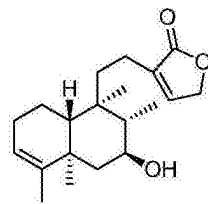
15



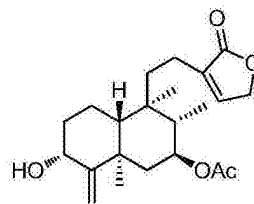
16



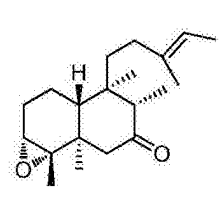
17



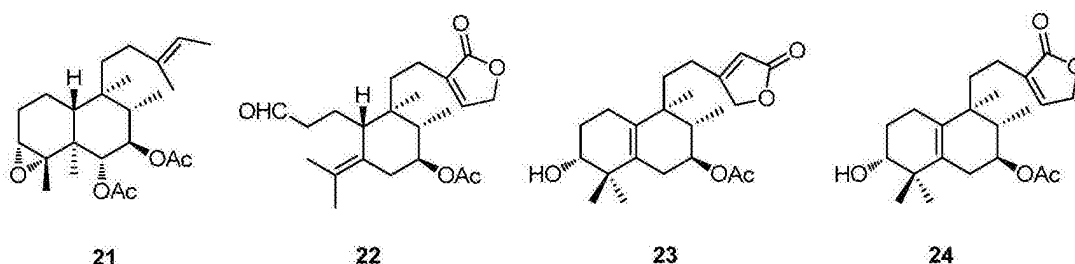
18



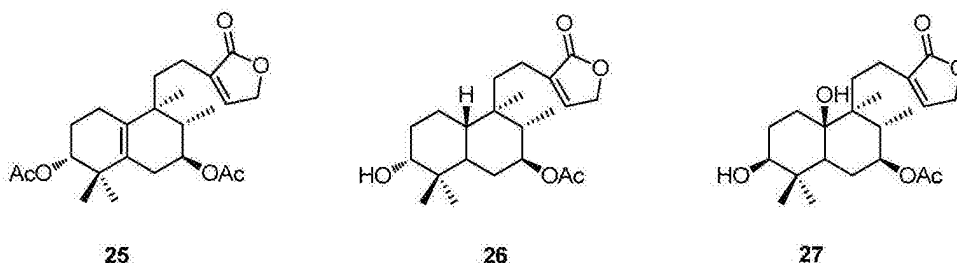
19



20



[0026]



[0027] 本发明化合物1-27的物理和光谱数据为:

[0028] 化合物1: Colorless blocks crystal; $[\alpha]_D^{14.8} = -5.60$ ($c=0.20$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 209 (3.45) nm; IR (KBr) ν_{\max} : 2979, 2968, 2928, 1776, 1743, 1639, 1373, 1248, 1016, 885, 869 cm^{-1} ; ESI-MS: m/z 457 $[M+Na]^+$; HR-EI-MS: m/z 434.2283 $[M]^+$ (calcd for $C_{24}H_{34}O_7$, 434.2305). ^1H and ^{13}C NMR 数据见表1和表2. ^1H and ^{13}C NMR 数据见表1和表2.

[0029] 化合物2: Colorless blocks crystal; $[\alpha]_D^{16.2} = -44.4$ ($c=0.12$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 209 (3.48) nm; IR (KBr) ν_{\max} : 3450, 2979, 2962, 2947, 2910, 1789, 1778, 1743, 1635, 1446, 1435, 1393, 1379, 1359, 1248, 1169, 1020, 1009, 978 cm^{-1} ; EI: m/z (%) 376 ($[M]^+$ 25), 306 (30), 261 (25), 108 (30), 87 (40), 85 (100), 83 (98), 79 (40); HR-EI-MS: m/z 376.2241 (calcd for $C_{22}H_{32}O_5$, 376.2250). ^1H and ^{13}C NMR 数据见表1和表2.

[0030] 化合物3: White solid; $[\alpha]_D^{15.8} = +10.5$ ($c=0.11$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 209 (3.62) nm; IR (KBr) ν_{\max} : 3436, 2970, 2934, 2881, 1789, 1780, 1748, 1637, 1451, 1377, 1363, 1248, 1172, 1143, 1025, 976, 886 cm^{-1} ; EI: m/z (%) 376 ($[M]^+$, 18), 316 (25), 306 (30), 187 (30), 149 (48), 95 (62), 93 (60), 79 (100), 67 (85), 55 (80); HR-EI-MS: m/z 376.2252 (calcd for $C_{22}H_{32}O_5$, 376.2250). ^1H and ^{13}C NMR 数据见表1和表2.

[0031] 化合物4: White solid; $[\alpha]_D^{14.7} = +6.5$ ($c=0.28$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 376 (1.08), 209 (3.54) nm; IR (KBr) ν_{\max} : 3473, 3440, 2980, 2960, 2926, 1786, 1744, 1730, 1637, 1463, 1452, 1382, 1374, 1245, 1169, 1150, 1028, 1016, 891, 852 cm^{-1} ; EI: m/z (%) 376 ($[M]^+$, 11), 317 (42), 316 (100), 301 (25), 209 (30), 205 (45), 150 (40), 149 (75), 133 (35), 107 (30), 55 (50); HR-EI-MS: m/z 376.2258 (calcd for $C_{22}H_{32}O_5$, 376.2250). ^1H and ^{13}C NMR 数据见表1和表2.

[0032] 化合物5: Colorless blocks crystal; $[\alpha]_D^{16.0} = -36.4$ ($c=0.15$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 210 (3.45) nm; IR (KBr) ν_{\max} : 3432, 2965, 2950, 2935, 2887, 1783, 1728, 1635, 1434, 1391, 1375, 1260, 1175, 1145, 1052, 1027, 1016, 976 cm^{-1} ; EI: m/z (%) 394 ($[M]^+$, 12), 293 (22), 224 (30), 149 (35), 85 (95), 83 (100), 69 (40), 59 (30); HR-EI-MS: m/z 394.2229 (calcd for $C_{22}H_{34}O_6$, 394.2355). ^1H and ^{13}C NMR 数据见表1和表2.

[0033] 化合物6:Colorless blocks crystal; $[\alpha]_D^{16.7}=+42.7$ ($c=0.11$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):208(3.54)$ nm; IR (KBr) $\nu_{\max}:3434, 2971, 2883, 1780, 1748, 1710, 1637, 1452, 1377, 1243, 1174, 1144, 1128, 1026, 971, 887$ cm^{-1} ; EI: m/z (%) 376 ($[M]^+$, 10), 255 (12), 185 (12), 149 (25), 120 (30), 118 (32), 87 (50), 85 (100), 83 (95), 59 (40); HR-EI-MS: m/z 376.2261 (calcd for $C_{22}H_{32}O_5$, 376.2250). ^1H and ^{13}C NMR数据见表3和表4。

[0034] 化合物7:White powder; $[\alpha]_D^{14.7}=-12.2$ ($c=0.30$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):208(3.43)$ nm; IR (KBr) $\nu_{\max}:3456, 2959, 2932, 1784, 1747, 1704, 1636, 1446, 1393, 1374, 1248, 1210, 1171, 1042, 1015, 976, 890$ cm^{-1} ; EI: m/z (%) 376 ($[M]^+$, 25), 316 (15), 245 (25), 219 (30), 206 (70), 205 (50), 147 (25), 133 (100), 95 (40), 55 (40); HR-EI-MS: m/z 376.2252 (calcd for $C_{22}H_{32}O_5$, 376.2250). ^1H and ^{13}C NMR数据见表3和表4。

[0035] 化合物8:White solid; $[\alpha]_D^{14.9}=-46.5$ ($c=0.09$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):207(3.13)$ nm; IR (KBr) $\nu_{\max}:3439, 2969, 2926, 2874, 1747, 1738, 1645, 1454, 1384, 1350, 1269, 1227, 1211, 1087, 1071, 1049, 882$ cm^{-1} ; EI: m/z (%) 332 ($[M]^+$, 25), 221 (35), 111 (30), 97 (48), 85 (60), 83 (85), 71 (75), 69 (70), 57 (100), 55 (90); HR-EI-MS: m/z 332.1987 (calcd for $C_{20}H_{28}O_4$, 332.1988). ^1H and ^{13}C NMR数据见表3和表4。

[0036] 化合物9:Colorless blocks crystal; $[\alpha]_D^{16.1}=-10.22$ ($c=0.12$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):208(3.36)$ nm; IR (KBr) $\nu_{\max}:3432, 2965, 2881, 1743, 1452, 1368, 1249, 1069, 1021, 986, 879$ cm^{-1} ; ESI-MS: m/z 457 $[M+Na]^+$; HR-EI-MS: m/z 434.2309 $[M]^+$ (calcd for $C_{24}H_{34}O_7$, 434.2305). ^1H and ^{13}C NMR数据见表3和表4。

[0037] 化合物10:Colorless blocks crystal; $[\alpha]_D^{15.9}=-245.87$ ($c=0.15$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):208(4.01)$ nm; IR (KBr) $\nu_{\max}:2977, 2952, 2938, 2910, 1754, 1743, 1725, 1453, 1393, 1378, 1251, 1232, 1080, 979$ cm^{-1} ; ESI-MS: m/z 399 $[M+Na]^+$; HR-EI-MS: m/z 376.2261 $[M]^+$ (calcd for $C_{22}H_{32}O_5$, 376.2250). ^1H and ^{13}C NMR数据见表3和表4。

[0038] 化合物11:White solid; $[\alpha]_D^{14.8}=-47.0$ ($c=0.32$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):208(3.40)$ nm; IR (KBr) $\nu_{\max}:3430, 2966, 2954, 2933, 1750, 1724, 1652, 1622, 1438, 1369, 1259, 1216, 1097, 1053, 1011, 977$ cm^{-1} ; EI: m/z (%) 394 ($[M]^+$, 15), 335 (35), 334 (100), 291 (45), 273 (90), 261 (100), 233 (45), 223 (52), 187 (50), 133 (67), 95 (70), 55 (80); HR-EI-MS: m/z 394.2340 (calcd for $C_{22}H_{34}O_6$, 394.2355). ^1H and ^{13}C NMR数据见表5和表6。

[0039] 化合物12:White solid; $[\alpha]_D^{14.7}=+17.5$ ($c=0.12$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):208(3.54)$ nm; IR (KBr) $\nu_{\max}:3434, 2964, 2954, 2933, 1758, 1747, 1652, 1638, 1438, 1374, 1248, 1216, 1024, 1015, 976$ cm^{-1} ; EI: m/z (%) 394 ($[M]^+$, 25), 336 (45), 334 (100), 291 (65), 261 (80), 223 (62), 187 (50), 95 (70), 55 (85); HR-EI-MS: m/z 394.2345 (calcd for $C_{22}H_{34}O_6$, 394.2355). ^1H and ^{13}C NMR数据见表5和表6。

[0040] 化合物13:Colorless blocks crystal; $[\alpha]_D^{15.2}=-74.8$ ($c=0.15$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):208(3.42)$ nm; IR (KBr) $\nu_{\max}:3510, 2950, 2932, 1753, 1739, 1454, 1442, 1395, 1370, 1255, 1072, 1048, 1021, 986$ cm^{-1} ; EI: m/z (%) 436 ($[M]^+$, 12), 376 (35), 344 (50), 316 (28), 275 (20), 265 (100), 233 (48), 205 (50), 187 (65), 91 (85), 55 (70); HR-EI-MS: m/z 436.2459 (calcd for $C_{24}H_{36}O_7$, 436.2461). ^1H and ^{13}C NMR数据见表5和表6。

[0041] 化合物14:White solid; $[\alpha]_D^{14.8}=-39.9$ ($c=0.10$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon):208$

(3.42)nm; IR(KBr) ν_{\max} : 3467, 2963, 1755, 1727, 1703, 1453, 1376, 1362, 1255, 1231, 1202, 1097, 1078, 1055, 1018, 977 cm^{-1} ; EI:m/z(%)392($[\text{M}]^+$, 62), 376(35), 332(30), 314(32), 289(50), 149(55), 135(100), 133(60), 112(65), 67(61), 55(75); HR-EI-MS:m/z392.2207 (calcd for $\text{C}_{22}\text{H}_{32}\text{O}_6$, 392.2199). ^1H and ^{13}C NMR数据见表5和表6。

[0042] 化合物15: White solid; $[\alpha]_{\text{D}}^{14.7} = -15.7$ (c=0.20, MeOH); UV(MeOH) $\lambda_{\max}(\log \epsilon)$: 208 (3.41)nm; IR(KBr) ν_{\max} : 3545, 2982, 2957, 1756, 1730, 1706, 1445, 1398, 1376, 1355, 1252, 1201, 1079, 1064, 1053, 1017, 976, 820 cm^{-1} ; EI:m/z(%)376($[\text{M}]^+$, 62), 376(15), 245(25), 205(50), 187(68), 147(45), 133(100), 67(62), 55(85); HR-EI-MS:m/z376.2255 (calcd for $\text{C}_{22}\text{H}_{32}\text{O}_5$, 376.2250). ^1H and ^{13}C NMR数据见表5和表6。

[0043] 化合物16: Colorless blocks crystal; $[\alpha]_{\text{D}}^{16.9} = -18.7$ (c=0.11, MeOH); UV(MeOH) $\lambda_{\max}(\log \epsilon)$: 210 (3.45)nm; IR(KBr) ν_{\max} : 3457, 3438, 3431, 3425, 2964, 2929, 1763, 1741, 1452, 1390, 1367, 1250, 1233, 1073, 1048, 1019, 992 cm^{-1} ; EI:m/z(%)418($[\text{M}]^+$, 12), 316(25), 298(30), 205(35), 187(60), 101(48), 85(100), 83(98), 59(80); HR-EI-MS:m/z418.2361 (calcd for $\text{C}_{24}\text{H}_{34}\text{O}_6$, 418.2355). ^1H and ^{13}C NMR数据见表7和表8。

[0044] 化合物17: White solid; $[\alpha]_{\text{D}}^{16.7} = -97.7$ (c=0.10, MeOH); UV(MeOH) $\lambda_{\max}(\log \epsilon)$: 205 (3.54)nm; IR(KBr) ν_{\max} : 3421, 2962, 2944, 2881, 1755, 1734, 1651, 1450, 1392, 1377, 1365, 1243, 1207, 1166, 1070, 1051, 1018, 977 cm^{-1} ; EI:m/z(%)360($[\text{M}]^+$, 14), 189(25), 120(40), 118(45), 87(85), 85(100), 83(50), 59(65); HR-EI-MS:m/z360.2291 (calcd for $\text{C}_{22}\text{H}_{32}\text{O}_4$, 360.2301). ^1H and ^{13}C NMR数据见表7和表8。

[0045] 化合物18: White solid; $[\alpha]_{\text{D}}^{16.4} = -86.6$ (c=0.12, MeOH); UV(MeOH) $\lambda_{\max}(\log \epsilon)$: 207 (3.42)nm; IR(KBr) ν_{\max} : 3459, 2959, 2936, 2876, 1748, 1650, 1449, 1380, 1348, 1206, 1077, 1054, 1003, 965, 830 cm^{-1} ; EI:m/z(%)318($[\text{M}]^+$, 18), 300(30), 285(25), 205(45), 190(48), 189(90), 119(40), 95(52), 85(90), 83(100), 69(40), 55(52); HR-EI-MS:m/z318.2197 (calcd for $\text{C}_{20}\text{H}_{30}\text{O}_3$, 318.2195). ^1H and ^{13}C NMR数据见表7和表8。

[0046] 化合物19: Colorless blocks crystal; $[\alpha]_{\text{D}}^{16.4} = -38.2$ (c=0.12, MeOH); UV(MeOH) $\lambda_{\max}(\log \epsilon)$: 207 (3.35)nm; IR(KBr) ν_{\max} : 3446, 2932, 2880, 1754, 1748, 1632, 1451, 1392, 1379, 1365, 1250, 1230, 1156, 1070, 1054, 1019, 973 cm^{-1} ; EI:m/z(%)376($[\text{M}]^+$, 10), 316(35), 187(25), 149(25), 101(40), 85(70), 83(100), 59(55), 55(42); HR-EI-MS:m/z376.2288 (calcd for $\text{C}_{20}\text{H}_{30}\text{O}_3$, 376.2250). ^1H and ^{13}C NMR数据见表7和表8。

[0047] 化合物20: White solid; $[\alpha]_{\text{D}}^{14.8} = -47.3$ (c=0.10, MeOH); UV(MeOH) $\lambda_{\max}(\log \epsilon)$: 216 (3.42)nm; IR(KBr) ν_{\max} : 3426, 2970, 2926, 2876, 1710, 1640, 1435, 1388, 1254, 1227, 1138, 1035, 883 cm^{-1} ; EI:m/z(%)304($[\text{M}]^+$, 18), 221(62), 138(100), 137(45), 109(48), 95(55), 85(90), 83(95), 69(72), 67(75), 55(73); HR-EI-MS:m/z304.2401 (calcd for $\text{C}_{20}\text{H}_{32}\text{O}_2$, 304.2402). ^1H and ^{13}C NMR数据见表7和表8。

[0048] 化合物21: White solid; $[\alpha]_{\text{D}}^{16.8} = -13.7$ (c=0.10, MeOH); UV(MeOH) $\lambda_{\max}(\log \epsilon)$: 212 (3.47)nm; IR(KBr) ν_{\max} : 3426, 2966, 1742, 1689, 1639, 1451, 1434, 1396, 1369, 1249, 1044, 1022, 986, 878 cm^{-1} ; EI:m/z(%)406($[\text{M}]^+$, 15), 298(25), 255(45), 199(30), 185(48), 122(35), 120(98), 118(100), 117(52); HR-EI-MS:m/z406.2722 (calcd for $\text{C}_{24}\text{H}_{38}\text{O}_5$, 406.2719). ^1H and ^{13}C NMR数据见表9和表10。

[0049] 化合物22: Colorless blocks crystal; $[\alpha]_D^{16.4} = -12.1$ ($c=0.13$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 205 (3.43) nm; IR (KBr) ν_{\max} : 3432, 2955, 2926, 2872, 1755, 1748, 1640, 1451, 1374, 1246, 1204, 1068, 1047, 1025, 979 cm^{-1} ; EI: m/z (%) 376 ($[M]^+$, 15), 316 (18), 283 (25), 273 (30), 272 (100), 229 (35), 217 (68), 85 (100), 83 (100); HR-EI-MS: m/z 376.2248, (calcd for $\text{C}_{22}\text{H}_{32}\text{O}_5$, 376.2250). ^1H and ^{13}C NMR数据见表9和表10。

[0050] 化合物23: Colorless blocks crystal; $[\alpha]_D^{16.1} = -55.6$ ($c=0.15$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 207 (3.44) nm; IR (KBr) ν_{\max} : 3471, 3451, 2971, 2936, 2882, 1780, 1747, 1637, 1460, 1383, 1366, 1249, 1172, 1131, 1059, 1027, 962, 886 cm^{-1} ; EI: m/z (%) 376 ($[M]^+$, 15), 316 (20), 293 (25), 233 (30), 188 (25), 187 (100), 149 (50), 119 (48), 85 (72), 83 (85), 59 (50); HR-EI-MS: m/z 376.2245, (calcd for $\text{C}_{22}\text{H}_{32}\text{O}_5$, 376.2250). ^1H and ^{13}C NMR数据见表9和表10。

[0051] 化合物24: White solid; $[\alpha]_D^{15.5} = -166.1$ ($c=0.11$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 204 (3.93) nm; IR (KBr) ν_{\max} : 3452, 2971, 2938, 2880, 1753, 1650, 1457, 1383, 1365, 1250, 1070, 1049, 1023, 974, 832 cm^{-1} ; ESI-MS: m/z 399 $[M+\text{Na}]^+$; HR-EI-MS: m/z 376.2242 $[M]^+$ (calcd for $\text{C}_{22}\text{H}_{32}\text{O}_5$, 376.2250). ^1H and ^{13}C NMR数据见表9和表10。

[0052] 化合物25: White solid; $[\alpha]_D^{16.5} = -79.6$ ($c=0.10$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 205 (3.53) nm; IR (KBr) ν_{\max} : 3435, 2972, 2937, 2856, 1755, 1732, 1638, 1459, 1372, 1248, 1071, 1045, 1023, 977 cm^{-1} ; EI: m/z (%) 418 ($[M]^+$, 10), 283 (20), 205 (25), 188 (30), 187 (100), 163 (25), 119 (25), 83 (25), 69 (25), 57 (25); HR-EI-MS: m/z 418.2352, (calcd for $\text{C}_{24}\text{H}_{34}\text{O}_6$, 418.2355). ^1H and ^{13}C NMR数据见表9和表10。

[0053] 化合物26: White solid; $[\alpha]_D^{16.8} = -96.3$ ($c=0.12$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 204 (3.47) nm; IR (KBr) ν_{\max} : 3447, 2963, 2932, 2872, 1753, 1651, 1450, 1374, 1351, 1247, 1073, 1052, 1023, 970, 902 cm^{-1} ; EI: m/z (%) 378 ($[M]^+$, 15), 358 (20), 316 (45), 283 (25), 237 (40), 223 (42), 205 (45), 188 (50), 187 (100), 95 (52), 145 (50), 119 (70), 91 (40), 55 (32); HR-EI-MS: m/z 378.2438 (calcd for $\text{C}_{22}\text{H}_{34}\text{O}_5$, 378.2406). ^1H and ^{13}C NMR数据见表11。

[0054] 化合物27: White solid; $[\alpha]_D^{16.9} = -19.9$ ($c=0.13$, MeOH); UV (MeOH) $\lambda_{\max}(\log \epsilon)$: 208 (3.48) nm; IR (KBr) ν_{\max} : 3429, 2986, 2968, 2936, 2926, 1755, 1724, 1471, 1458, 1384, 1368, 1347, 1253, 1212, 1061, 1030, 1005, 979, 831 cm^{-1} ; EI: m/z (%) 394 ($[M]^+$, 18), 317 (30), 316 (65), 301 (45), 273 (25), 206 (62), 205 (100), 191 (30), 119 (45), 83 (52), 67 (40), 55 (38); HR-EI-MS: m/z 394.2346 (calcd for $\text{C}_{22}\text{H}_{34}\text{O}_6$, 394.2355). ^1H and ^{13}C NMR数据见表11。

[0055] 表1、化合物1-5的 ^1H NMR数据^a

[0056]

| position | 1 ^b | 2 ^c | 3 ^c | 4 ^c | 5 ^c |
|----------|--------------------------|--------------------------|--------------------------|----------------------|--------------------------|
| 1 | 1.38, overlap | 1.27, m 1.33, m | 1.22, m 1.31, m | 1.32, m | 1.34, m 1.74, overlap |
| 2 | 1.85, m 2.02, overlap | 1.80, m 2.02, overlap | 1.81, m 2.03, overlap | 1.83, m 2.00, m | 1.63, m 2.04, overlap |
| 3 | 2.83, brs | 2.88, brs | 2.88, brs | 2.81, brs | 3.58, brs |
| 4 | | | | | 2.40, m |
| 6 | 4.95, d (4.1) | 1.73, m 2.00, overlap | 1.43, m 1.98, m | 4.80, dd (11.1, 4.7) | 1.73, overlap 2.05, m |
| 7 | 5.35, t (3.6) | 5.11, brs | 4.91, td (11.2, 4.2) | 1.53, m 1.67, m | 5.09, d (2.9) |
| 8 | 2.02, overlap | 1.83, m | 1.19, overlap | 1.75, m | 1.70, m |
| 10 | 1.38, overlap | 1.18, m | 1.65, overlap | 1.15, overlap | 2.02, overlap |
| 11 | 1.63, m 1.70, m | 1.61, m 1.70, m | 1.64, overlap 1.71, m | 1.61, m 1.68, m | 1.59, m 1.72, overlap |
| 12 | 2.32, m 2.47, m | 2.27, m 2.39, m | 2.31, m 2.46, m | 2.27, m 2.45, m | 2.35, m |
| 14 | 5.89, s | 5.89, s | 5.89, brs | 5.88, brs | 5.89, brs |
| 15 | | | | | 4.88, d (1.4) |
| 16 | 4.85, s | 4.85, brs | 4.85, brs | 4.84, d (1.7) | 7.40, s |
| 17 | 0.87, d (7.0) | 0.88, d (6.9) | 0.83, d (6.6) | 0.81, d (6.8) | 0.90, d (7.0) |
| 18 | 1.09, s | 1.12, s | 1.12, s | 1.10, s | 1.20, s |
| 19 | 1.34, s | 1.21, s | 1.10, s | 1.13, s | 1.36, s |
| 20 | 0.96, s | 0.95, s | 0.78, s | 0.71, s | 1.06, s |
| 3-OH | | | | | 3.81, d (3.9) |
| 4-OH | | | | | 3.32, brs |
| 6-OAc | 2.08, s | | | | |
| 7-OAc | 1.95, s | 2.03, s | 2.01, s | 2.03, s | 2.01, s |

[0057] ^a Bruker DRX-400MHz或500MHz核磁共振仪测定,化学位移值(δ_H)用ppm表示,耦合常数J用Hz表示;^b以CDCl₃为溶剂;^c以Acetone-d₆为溶剂。

[0058] 表2、化合物1-5的¹³C NMR数据^a

[0059]

| position | 1 ^b | 2 ^c | 3 ^c | 4 ^c | 5 ^c |
|----------|----------------|----------------|----------------|----------------|----------------|
| 1 | 15.1, t | 15.7, t | 15.9, t | 15.3, t | 17.1, t |
| 2 | 28.3, t | 28.8, t | 28.5, t | 28.3, t | 31.4, t |
| 3 | 63.3, d | 62.3, d | 62.2, d | 63.2, d | 76.6, d |
| 4 | 65.8, s | 66.2, s | 65.8, s | 65.7, s | 75.9, s |
| 5 | 42.0, s | 37.0, s | 38.3, s | 42.4, s | 41.6, s |
| 6 | 75.6, d | 40.7, t | 43.0, t | 77.2, d | 36.5, t |
| 7 | 74.6, d | 75.2, d | 74.0, d | 34.1, d | 76.3, d |
| 8 | 37.2, d | 38.4, d | 47.9, d | 34.6, d | 38.3, d |
| 9 | 39.2, s | 39.4, s | 40.6, s | 39.3, s | 38.9, s |
| 10 | 47.0, d | 48.2, d | 41.5, d | 47.0, d | 41.1, d |
| 11 | 37.0, t | 36.9, t | 36.1, t | 35.9, t | 37.3, t |
| 12 | 22.7, t | 22.9, t | 22.7, t | 22.5, t | 23.0, t |
| 13 | 174.1, s | 172.8, s | 172.7, s | 174.3, s | 173.2, s |
| 14 | 115.0, d | 114.9, d | 114.9, d | 114.9, d | 114.8, d |
| 15 | 172.7, s | 174.3, s | 174.3, s | 172.9, s | 73.8, t |
| 16 | 73.7, t | 73.7, t | 73.7, t | 74.0, t | 146.2, d |
| 17 | 11.8, q | 12.3, q | 11.3, q | 15.8, q | 12.6, q |
| 18 | 21.5, q | 19.9, q | 19.8, q | 21.6, q | 21.5, q |
| 19 | 13.8, q | 17.9, q | 17.9, q | 13.9, q | 19.0, q |

[0060]

| | | | | | |
|-------|----------|----------|----------|----------|----------|
| 20 | 19.5, q | 20.0, q | 19.8, q | 18.2, q | 20.1, q |
| 6-OAc | 171.0, s | | | | 170.7, s |
| | 20.8, q | | | | 21.3, q |
| 7-OAc | 170.4, s | 170.5, s | 170.6, s | 170.6, s | |
| | 21.3, q | 21.3, q | 21.1, q | 21.7, q | |

[0061] ^a Bruker DRX-100MHz或125MHz核磁共振仪测定,化学位移值(δ_c)用ppm表示;^b以CDCl₃为溶剂;^c以Acetone-d₆为溶剂。

[0062] 表3、化合物6-10的¹H NMR数据^a

[0063]

| position | 6 | 7 | 8 | 9 | 10 |
|----------|---------------|--------------------|---------------|---------------|---------------------|
| 1 | 1.76, overlap | 1.69, m | 1.28, m | 1.36, overlap | 1.28, m |
| | 2.00, overlap | 1.78, m | 1.43, m | 1.44, m | 1.39, m |
| 2 | 2.26, m | 1.59, m | 1.91, m | 1.86, m | 1.80, m |
| | 2.45, m | 2.00, overlap | 2.10, m | 2.04, m | 2.03, m |
| 3 | 2.81, brs | 2.88, brs | 2.98, brs | 2.84, t (6.7) | 2.89, s |
| 4 | 2.45, overlap | 2.36, m | 2.40, m | | |
| 6 | 1.32, m | 2.26, m | 2.27, m | 4.98, d (4.1) | 1.78, m |
| | 1.95, overlap | 2.45, m | 2.75, m | | 2.00, m |
| 7 | 4.85, m | 5.09 dd (6.4, 3.2) | | 5.36, t (3.7) | 5.13, dd (6.7, 3.6) |
| 8 | 1.75, overlap | 1.93, m | 2.70, m | 2.03, overlap | 1.86, m |
| 10 | 1.97, overlap | 2.01, overlap | 1.83, m | 1.36, overlap | 1.22, overlap |
| 11 | 1.76, overlap | 1.82, m | 1.51, m | 1.51, m | 1.50, m |
| | | 2.05, m | 1.74, m | 1.59, m | 1.58, m |
| 12 | 2.55, m | 2.50, m | 2.24, m | 2.06, m | 2.02, m |
| | | 2.57, m | | 2.20, m | 2.13, m |
| 14 | 5.92, brs | 5.90, brs | 5.89, brs | 7.43, s | 7.40, brs |
| 15 | | | 4.80, d (1.8) | 4.79, brs | 4.79, brs |
| 16 | 4.90, brs | 4.88, brs | 7.45, brs | | |
| 17 | 0.90, d (6.7) | 0.94, d (7.0) | 0.89, d (6.7) | 0.89, d (7.0) | 0.90, d (7.0) |
| 18 | 0.84, d (6.1) | 0.82, d (6.7) | 1.15, s | 1.10, s | 1.13, s |
| 19 | 0.83, s | 0.90, s | 0.92, s | 1.34, s | 1.22, s |
| 20 | 0.92, s | 1.07, s | 0.63, s | 0.93, s | 0.92, s |
| 6-OAc | | | | 1.94, s | |
| 7-OAc | 2.03, s | 2.01, s | | 2.08, s | 2.03, s |

[0064] ^a Bruker DRX-400MHz或500MHz核磁共振仪测定,化学位移值(δ_H)用ppm表示,耦合常数J用Hz表示;以Acetone-d₆为溶剂。

[0065] 表4、化合物6-10的¹³C NMR数据^a

[0066]

| position | 6 | 7 | 8 | 9 | 10 |
|----------|----------|----------|----------|----------|----------|
| 1 | 23.2, t | 37.0, t | 16.3, t | 15.1, t | 15.7, t |
| 2 | 41.5, t | 42.2, t | 28.5, t | 28.4, t | 28.8, t |
| 3 | 210.8, s | 211.1, s | 62.3, d | 63.4, d | 62.3, d |
| 4 | 57.8, d | 58.6, d | 65.6, s | 66.0, s | 66.3, s |
| 5 | 42.8, s | 41.2, s | 42.0, s | 42.0, s | 37.0, s |
| 6 | 44.8, t | 41.7, t | 53.3, t | 75.7, d | 40.7, t |
| 7 | 72.9, d | 75.2, d | 211.7, s | 74.8, d | 75.3, d |
| 8 | 41.9, d | 38.4, d | 50.1, d | 37.4, d | 38.5, d |
| 9 | 41.0, s | 39.3, s | 44.6, s | 39.2, s | 39.2, s |
| 10 | 48.5, d | 48.5, d | 47.7, d | 47.0, d | 48.3, d |
| 11 | 36.2, t | 23.3, t | 37.5, t | 38.0, t | 37.8, t |
| 12 | 22.6, t | 22.9, t | 20.1, t | 19.7, t | 19.8, t |
| 13 | 174.6, s | 172.9, s | 133.7, s | 134.0, s | 134.0, s |
| 14 | 115.0, d | 115.0, d | 174.7, s | 146.4, d | 146.3, d |

[0067]

| | | | | | |
|-------|----------|----------|----------|----------|----------|
| 15 | 172.9, s | 174.3, s | 71.0, t | 71.0, t | 71.0, t |
| 16 | 73.7, t | 73.7, t | 146.5, d | 174.7, s | 174.7, s |
| 17 | 19.3, q | 12.4, q | 8.2, q | 11.8, q | 12.2, q |
| 18 | 7.3, q | 7.3, q | 19.8, q | 21.5, q | 19.9, q |
| 19 | 15.4, q | 16.3, q | 18.2, q | 13.8, q | 18.0, q |
| 20 | 10.8, q | 19.9, q | 19.7, q | 19.6, q | 20.0, q |
| 6-OAc | | | | 170.4, s | |
| | | | | 21.3, q | |
| 7-OAc | 170.6, s | 170.5, s | | 170.9, s | 170.5, s |
| | 20.9, q | 21.2, q | | 20.9, q | 21.3, q |

[0068] ^a Bruker DRX-100MHz或125MHz核磁共振仪测定,化学位移值(δ_c)用ppm表示;以Acetone-d₆为溶剂。

[0069] 表5、化合物11-15的¹H NMR数据^a

[0070]

| position | 11 | 12 | 13 | 14 | 15 |
|----------|--------------------------|--------------------------|--------------------------------|--------------------------|--------------------------------|
| 1 | 1.40, m 1.72, overlap | 1.69, m | 1.48, m 1.60, overlap | 1.72, overlap 1.99, m | 1.81, m 2.11, m |
| 2 | 1.58, m 1.70, overlap | 1.65, overlap 1.86, m | 1.62, overlap 2.08, overlap | 1.58, m 1.70, overlap | 1.61, overlap 2.00, overlap |
| 3 | 3.57, brs | 3.85, brs | 4.73, brs | 2.83, brs | 2.84, t (6.7) |
| 4 | | 2.40, m | | | 2.40, m |
| 6 | 1.72, overlap 2.08, m | 1.62, overlap 2.03, m | 1.72, overlap 2.07, overlap | 5.17, dd (6.5,3.2) | 2.28, m 2.48, m |
| 7 | 5.09, d (2.5) | 5.07, d (2.9) | 5.11, d (2.8) | 1.73, overlap 2.17, m | 5.10, d (2.9) |
| 8 | 1.73, overlap | 1.70, m | 1.76, overlap | 1.87, m | 1.94, m |
| 10 | 2.05, overlap | 2.07, m | 2.10, m | 2.69, m | 2.02, overlap |
| 11 | 1.48, m 1.63, m | 1.47, m 1.62, m | 1.51, m 1.61, overlap | 2.14, m 3.06, m | 1.58, m 1.68, m |
| 12 | 2.12, m | 2.11, m | 2.12, m | 2.24, m 2.28, m | 2.28, m |
| 14 | 5.89, s | | 5.89, s | 5.89, s | |
| 15 | 4.79, brs | 4.79, d (1.6) | 4.78, brs | 4.83, dd (3.4,1.7) | 4.80, brs |
| 16 | 7.40, s | 7.40, s | 7.40, s | 7.44, s | 7.44, s |
| 17 | 0.90, d (7.0) | 0.89, d (7.0) | 0.91, d (7.0) | 0.97, d (7.2) | 0.95, d (7.0) |
| 18 | 1.19, s | 1.14, s | 1.07, s | 1.10, s | 0.82, d (6.6) |
| 19 | 1.32, s | 1.36, s | 1.30, s | 0.97, s | 1.04, s |
| 20 | 1.02, s | 1.01, s | 1.02, s | 1.06, s | 0.90, s |
| 3-OAc | | | 2.02, s | | |
| 6-OAc | | | | 2.03, s | |
| 7-OAc | 1.99, s | 1.98, s | 2.00, s | | 2.01, s |
| 3-OH | 3.78, d (3.9) | 3.74, d (4.3) | | | |
| 4-OH | 3.30, brs | | 3.76, brs | 4.57, s | |

[0071] ^a Bruker DRX-400MHz或500MHz核磁共振仪测定,化学位移值(δ_{H})用ppm表示,耦合常数J用Hz表示;Acetone-d₆为溶剂。

[0072] 表6、化合物11-15的¹³C NMR数据^a

[0073]

| position | 11 | 12 | 13 | 14 | 15 |
|----------|---------|---------|---------|----------|----------|
| 1 | 17.1, t | 16.8, t | 17.3, t | 22.9, t | 23.3, t |
| 2 | 31.4, t | 31.5, t | 38.1, t | 38.1, t | 42.2, t |
| 3 | 76.7, d | 70.1, d | 77.5, d | 212.5, s | 211.2, d |
| 4 | 76.0, s | 80.1, s | 75.1, s | 80.9, s | 58.5, d |
| 5 | 41.6, s | 42.7, s | 41.6, s | 43.8, s | 41.1, s |

[0074]

| | | | | | |
|-------|----------|----------|----------|----------|----------|
| 6 | 36.6, t | 36.2, t | 36.1, t | 76.2, d | 41.8, t |
| 7 | 76.5, d | 76.4, d | 76.5, d | 35.4, t | 75.3, d |
| 8 | 38.4, d | 38.4, d | 38.3, d | 38.4, d | 38.5, d |
| 9 | 38.9, s | 38.9, s | 38.8, s | 39.3, s | 39.2, s |
| 10 | 41.1, d | 40.6, d | 40.6, d | 39.0, d | 48.5, d |
| 11 | 38.1, t | 38.1, t | 37.9, t | 37.7, t | 37.8, t |
| 12 | 20.0, t | 20.0, t | 19.9, t | 20.1, t | 19.8, t |
| 13 | 134.3, s | 134.3, s | 134.1, s | 134.1, s | 134.1, s |
| 14 | 174.8, s | 174.7, s | 174.7, s | 175.2, s | 174.8, s |
| 15 | 71.0, t | 71.0, t | 70.9, t | 71.1, t | 71.0, t |
| 16 | 146.1, d | 146.2, d | 146.2, d | 146.5, d | 146.4, d |
| 17 | 12.6, q | 12.6, q | 12.5, q | 12.5, q | 16.3, q |
| 18 | 21.6, q | 14.3, q | 20.8, q | 16.6, q | 7.3, q |
| 19 | 19.1, q | 19.5, q | 18.5, q | 18.3, q | 19.9, q |
| 20 | 20.2, q | 20.4, q | 20.1, q | 20.1, q | 12.3, q |
| 3-OAc | | | 170.1, s | | |
| | | | 21.3, q | | |
| 6-OAc | | | | 170.7, s | |
| | | | | 21.4, q | |
| 7-OAc | 170.6, s | 170.6, s | 170.6, s | | 170.5, s |
| | 21.3, q | 21.4, q | 21.3, q | | 21.2, q |

[0075] ^a Bruker DRX-100MHz或125MHz核磁共振仪测定,化学位移值(δ_c)用ppm表示;以Acetone-d₆为溶剂。

[0076] 表7、化合物16-20的¹H NMR数据^a

[0077]

| position | 16 | 17 | 18 | 19 | 20 |
|----------|--------------------------|--------------------------------|--------------------|--------------------------|----------------------------------|
| 1 | 1.71, m 1.79, m | 1.63, m 1.74, overlap | 1.50, m 1.70, m | 1.58, overlap 1.92, m | 1.30, m 1.40, m |
| 2 | 2.05, m | 2.04, m | 2.03, m | 1.58, overlap 1.96, m | 1.92, m 2.10, m |
| 3 | 5.18, brs | 5.41, brs | 5.11, brs | 4.27, brs | 3.29, brs |
| 4 | | 2.40, m | 2.40, m | | |
| 6 | 4.75, d (4.0) | 1.44, m 2.06, overlap | 1.39, m 2.11, m | 1.72, m 2.10, overlap | 2.27, d (11.6) 2.74, d (11.1) |
| 7 | 5.30, t (3.6) | 5.10, dd (6.5, 3.4) | 4.01, m | 5.14, d (3.1) | 4.91, td (11.2, 4.2) |
| 8 | 2.02, m | 1.82, m | 1.61, m | 1.83, m | 2.68, overlap |
| 9 | | | | | |
| 10 | 1.62, overlap | 1.52, overlap | 1.48, m | 1.27, m | 1.78, m |
| 11 | 1.54, m 1.63, overlap | 2.11, m | 1.52, m 1.60, m | 1.53, m 1.63, m | 1.41, m 1.65, m |
| 12 | 2.16, m | 1.54, overlap 1.64, overlap | 2.10, m | 2.07, m | 2.16, overlap |
| 14 | 7.42, s | 5.89, brs | 5.89, brs | 7.41, brs | 5.73, brs |
| 15 | 4.79, d (1.4) | 4.78, d (1.7) | 4.78, d (1.7) | 4.79, brs | 2.08, overlap |
| 16 | | 7.41, brs | 7.39, brs | | 2.16, s |
| 17 | 0.91, d (7.0) | 0.92, d (7.1) | 1.04, d (6.7) | 0.93, d (7.0) | 0.88, d (6.7) |
| 18 | 1.57, s | 1.57, s | 1.59, s | 4.71, s 4.79, s | 1.14, s |
| 19 | 1.34, s | 1.21, s | 1.31, s | 1.47, s | 0.92, s |
| 20 | 1.02, s | 1.00, s | 1.03, s | 1.05, s | 0.64, s |
| 6-OAc | 1.92, s | | | | |
| 7-OAc | 2.07, s | 2.02, s | | 2.01, s | |
| 3-OH | | | 3.57, d (3.7) | 3.65, brs | |

[0078] ^a Bruker DRX-400MHz或500MHz核磁共振仪测定,化学位移值(δ_{H})用ppm表示,耦合常数J用Hz表示;以Acetone-d₆为溶剂。

[0079] 表8、化合物16-20的¹³C NMR数据^a

[0080]

| position | 16 | 17 | 18 | 19 | 20 |
|----------|----------|----------|----------|----------|----------|
| 1 | 17.8, t | 18.4, t | 18.5, t | 17.1, t | 16.3, t |
| 2 | 26.9, t | 27.2, t | 27.3, t | 35.9, t | 28.4, t |
| 3 | 123.0, s | 120.8, d | 120.3, d | 74.1, d | 62.3, d |
| 4 | 143.6, s | 144.9, s | 145.6, s | 161.5, s | 65.6, s |
| 5 | 42.7, s | 38.0, s | 38.5, s | 40.1, s | 42.0, s |
| 6 | 76.3, d | 40.4, t | 44.0, t | 41.7, t | 53.3, t |
| 7 | 75.0, d | 75.5, d | 73.2, d | 75.4, d | 211.6, s |
| 8 | 37.5, d | 39.0, d | 40.1, d | 38.6, d | 50.0, d |
| 9 | 38.9, s | 38.5, s | 39.0, s | 39.5, s | 44.7, s |
| 10 | 46.2, d | 47.0, d | 47.5, d | 49.3, d | 47.7, d |
| 11 | 37.9, t | 19.8, t | 38.0, t | 37.8, t | 37.9, t |
| 12 | 19.6, t | 37.8, t | 19.7, t | 19.8, t | 35.4, t |
| 13 | 134.0, s | 134.2, s | 134.4, s | 134.1, s | 161.2, s |
| 14 | 146.4, d | 174.7, s | 174.7, s | 146.2, d | 116.5, d |
| 15 | 70.9, t | 73.8, t | 73.8, t | 70.9, t | 29.8, q |
| 16 | 174.7, s | 146.3, d | 146.0, d | 174.7, s | 18.2, q |
| 17 | 11.9, q | 12.4, q | 13.1, q | 12.4, q | 8.3, q |
| 18 | 21.3, q | 18.3, q | 18.3, q | 108.8, t | 19.8, q |
| 19 | 17.5, q | 21.8, q | 22.1, q | 24.2, q | 16.4, q |
| 20 | 19.5, q | 20.0, q | 20.3, q | 20.0, q | 19.8, q |
| 6-OAc | 170.3, s | | | | |
| | 21.1, q | | | | |
| 7-OAc | 171.0, s | 170.5, s | | 170.6, s | |
| | 20.9, q | 21.3, q | | 21.2, q | |

[0081] ^a Bruker DRX-100MHz或125MHz核磁共振仪测定,化学位移值(δ_c)用ppm表示;以Acetone-d₆为溶剂。

[0082] 表9、化合物21-25的¹H NMR数据^a

[0083]

| position | 21 | 22 | 23 | 24 | 25 |
|----------|--------------------------------|--------------------------|--------------------------------|--------------------------------|--------------------------|
| 1 | 1.36, overlap 1.42, overlap | 1.88, m 2.04, m | 1.66, m 1.78, overlap | 1.67, overlap 1.76, overlap | 2.07, overlap 2.20, m |
| 2 | 1.90, m 2.09, m | 2.30, m | 1.95, m 2.25, overlap | 1.99, overlap 2.24, m | 1.80, overlap |
| 3 | 2.84, brs | 9.69, brs | 3.45, m | 3.45, brs | 4.72, brs |
| 4 | | | | | 2.40, m |
| 6 | 4.93, d (4.1) | 2.17, m 2.62, m | 2.14, m 2.27, m | 2.13, m 2.27, overlap | 2.14, m 2.31, m |
| 7 | 5.35 d (3.7) | 4.89, dt (12.5,4.8) | 5.10, m | 5.11, brs | 5.14, brs |
| 8 | 2.04, overlap | 2.00, overlap | 1.99, m | 1.99, overlap | 2.07, overlap |
| 10 | 1.37, overlap | 2.36, m | | 1.27, m | 1.83, m |
| 11 | 1.45, overlap 1.51, m | 1.44, m 1.74, overlap | 1.73, overlap 1.83, overlap | 1.62, overlap 1.73, overlap | 1.69, m 1.77, overlap |
| 12 | 2.00, m 2.15, overlap | 1.26, m 2.16, m | 2.43, m | 2.17, overlap | 2.19, m 2.29, m |
| 14 | 5.71, brs | 7.32, brs | 5.86, brs | | |
| 15 | 2.08, overlap | 4.79, d (1.7) | | 4.78, brs | 4.78, brs |
| 16 | 2.15, s | | 4.84, brs | 7.37, brs | 7.39, brs |
| 17 | 0.88, d (6.9) | 1.07, d (7.4) | 0.86, d (6.9) | 0.87, d (6.8) | 0.88, d (6.6) |
| 18 | 1.09, q | 1.68, s | 1.02, s | 1.02, s | 1.02, s |
| 19 | 1.33, q | 1.74, s | 0.98, s | 0.97, s | 0.99, s |
| 20 | 0.94, q | 1.13, s | 1.04, s | 1.03, s | 1.05, s |
| 3-OAc | | | | | 1.99, s |
| 6-OAc | 1.94, s | | | | |

[0084]

| | | | | | |
|-------|---------|---------|---------------|---------------|---------|
| 7-OAc | 2.08, s | 2.01, s | 1.99, s | 2.01, s | 2.00, s |
| 3-OH | | | 3.55, d (5.2) | 3.55, d (4.9) | |

[0085] ^a Bruker DRX-500MHz核磁共振仪测定,化学位移值(δ_{H})用ppm表示,耦合常数J用Hz表示;以Acetone-d₆为溶剂。

[0086] 表10、化合物21-25的¹³C NMR数据^a

[0087]

| position | 21 | 22 | 23 | 24 | 25 |
|----------|----------|----------|----------|----------|----------|
| 1 | 19.8, t | 23.3, t | 27.6, t | 28.1, t | 22.7, t |
| 2 | 28.5, t | 43.6, t | 22.8, t | 23.4, t | 24.3, t |
| 3 | 63.5, d | 202.9, s | 74.9, d | 75.5, d | 77.7, d |
| 4 | 66.0, s | 129.2, s | 40.0, s | 40.5, s | 38.7, s |
| 5 | 42.0, s | 129.0, s | 132.4, s | 132.6, s | 131.4, s |
| 6 | 75.8, d | 26.4, t | 28.9, t | 29.5, t | 28.7, t |
| 7 | 74.8, d | 73.0, d | 72.0, d | 72.6, d | 71.8, s |
| 8 | 37.3, d | 38.9, d | 36.5, d | 37.0, d | 36.6, d |
| 9 | 39.4, s | 41.4, s | 42.4, s | 42.7, s | 42.5, s |
| 10 | 47.1, d | 47.2, d | 132.1, s | 132.8, s | 133.0, s |
| 11 | 38.4, t | 39.7, t | 37.3, t | 38.3, t | 37.9, t |
| 12 | 35.1, t | 20.7, t | 23.9, t | 21.3, t | 20.9, t |
| 13 | 161.6, s | 134.3, s | 173.0, s | 134.8, s | 134.3, s |
| 14 | 117.7, d | 146.1, d | 115.0, d | 175.2, s | 174.8, s |
| 15 | 29.9, q | 70.9, t | 174.2, s | 71.5, t | 71.1, t |
| 16 | 15.2, q | 174.6, s | 73.7, d | 146.7, d | 146.4, d |
| 17 | 12.0, q | 10.7, q | 10.6, q | 11.4, q | 10.6, q |
| 18 | 21.6, q | 21.1, q | 26.7, q | 27.2, q | 26.6, q |
| 19 | 13.9, q | 20.7, q | 21.8, q | 22.2, q | 22.3, q |
| 20 | 18.9, q | 21.4, q | 22.1, q | 22.8, q | 22.3, q |
| 3/6-OAc | 170.5, s | | | | 170.9, s |
| | 21.4, q | | | | 21.1, s |
| 7-OAc | 171.1, s | 170.4, s | 171.0, s | 171.4, s | 170.8, s |
| | 21.0, q | 20.9, q | 21.2, q | 21.8, q | 21.3, q |

[0088] ^a Bruker DRX-100MHz或125MHz核磁共振仪测定,化学位移值(δ_C)用ppm表示,耦合常数J用Hz表示;^b以Acetone-d₆为溶剂。

[0089] 表11、化合物26和27的¹H和¹³C NMR数据^a

[0090]

| position | 26 | | 27 | |
|----------|--------------------------|------------|--------------------------|------------|
| | δ_H | δ_C | δ_H | δ_C |
| 1 | 1.80, m 2.04, m | 20.2, t | 1.44, m 1.65, m | 28.1, t |
| 2 | 1.57, m 1.80, m | 20.3, t | 1.38, m 1.72, overlap | 31.2, t |
| 3 | 3.50, brs | 78.5, d | 3.77, d (4.6) | 87.1, d |
| 4 | 2.40, m | 41.7, s | | 43.9, s |
| 5 | 2.12, m | 41.9, d | 1.74, overlap | 51.6, d |
| 6 | 1.50, m 1.62, m | 30.1, t | 1.31, m 1.82, m | 26.2, t |
| 7 | 5.26, brs | 72.3, s | 5.03, dt (11.9,4.1) | 71.9, d |
| 8 | 1.91, overlap | 36.6, d | 2.02, m | 36.8, d |
| 9 | | 41.4, s | | 41.6, s |
| 10 | 2.26, m | 40.9, d | | 91.3, s |
| 11 | 1.67, m 1.94, overlap | 28.7, t | 1.48, m 1.90, m | 36.2, t |
| 12 | 2.18, m 2.31, m | 20.2, t | 2.16, m 2.51, m | 20.1, t |
| 13 | | 134.3, s | | 134.4, s |

[0091]

| | | | | |
|-------|---------------|----------|---------------|----------|
| 14 | | 174.7, s | | 174.5, s |
| 15 | 4.79, brs | 71.0, t | 4.79, brs | 70.9, t |
| 16 | 7.40, brs | 146.1, d | 7.38, brs | 146.2, d |
| 17 | 0.93, d (6.6) | 11.0, q | 1.06, d (6.7) | 9.3, q |
| 18 | 1.05, s | 28.4, q | 1.04, s | 27.3, q |
| 19 | 0.90, s | 26.0, q | 0.99, s | 25.9, q |
| 20 | 1.15, s | 25.9, q | 1.07, s | 18.6, q |
| 7-OAc | | 170.9, s | | 170.6, s |
| | 1.99, s | 21.1, q | 1.99, s | 21.2, q |
| 3-OH | 3.42, d (3.9) | | 3.55, d (4.9) | |

[0092] ¹H NMR, Bruker DRX-400MHz核磁共振仪测定¹³C NMR, Bruker DRX-100MHz核磁共振仪测定¹³C NMR, 化学位移值(δ_H 和 δ_C)用ppm表示, 以Acetone-d₆为溶剂。

[0093] 实施例3:

[0094] 本发明化合物1-27的拒食活性检测:

[0095] 采用叶碟法测试本发明化合物1-27对甜菜夜蛾(*Spodoptera exigua*), 斜纹夜蛾(*Spodoptera litura*)和棉铃虫(*Helicoverpa armigera*)的拒食活性。活性测试之前将2-3龄左右生长比较一致的幼虫, 饥饿处理4-5小时。选取生长一致的小白菜(*Brassica chinensis*)叶, 冲洗干净, 用打孔器(直径1.1cm)打制成圆叶片(叶碟)。将本发明化合物用丙酮配置成5种不同浓度梯度, 取10 μ L滴在叶碟上, 晾干, 即为处理叶碟; 对照叶碟为直接取丙酮溶液10 μ L滴在叶碟上, 晾干, 然后再将2片处理叶碟和2片对照叶碟交错放入一个直径9cm的培养皿内并且每个培养皿中放2头幼虫。为防止叶碟干缩, 在培养皿底垫一层滤纸, 滴加蒸馏水保湿。待取食24小时后, 将残存叶片取出, 用坐标纸测量对照叶碟和处理叶碟被试虫取食的面积。拒食率=[(C-T)/(C+T)] \times 100。用几率值法计算拒食中浓度EC₅₀(μ g/cm²)。大部分化合物拒食中浓度都高于阳性对照, 显示这些化合物具有很强的植食性昆虫拒食活性。活性数据见表12。

[0096] 表12、化合物1-27的拒食活性数据

[0097]

| 化合物 | EC ₅₀ (μ g/cm ²) | | |
|-----|--|-------|-------|
| | 甜菜夜蛾 | 棉铃虫 | 斜纹夜蛾 |
| 1 | 0.22 | 3.24 | 12.74 |
| 2 | 5.75 | 7.21 | 10.02 |
| 3 | 6.92 | 8.32 | 16.21 |
| 4 | 1.84 | 11.23 | 3.97 |
| 5 | 1.40 | 9.36 | 2.87 |
| 6 | 1.821 | 13.22 | 4.95 |
| 7 | 1.93 | 15.49 | 2.21 |
| 8 | 10.32 | 1.99 | 12.31 |
| 9 | 14.72 | 2.89 | 8.88 |

[0098]

| | | | |
|-------------------|-------|-------|-------|
| 10 | 10.02 | 3.43 | 9.36 |
| 11 | 13.44 | 3.26 | 17.65 |
| 12 | 10.18 | 2.58 | 12.47 |
| 13 | 9.90 | 2.27 | 7.11 |
| 14 | 8.63 | 7.14 | 13.21 |
| 15 | 2.97 | 14.89 | 1.22 |
| 16 | 27.91 | 3.56 | 16.93 |
| 17 | 35.69 | 9.91 | 25.25 |
| 18 | 11.18 | 3.52 | 14.23 |
| 19 | 5.09 | 1.35 | 9.42 |
| 20 | 60.26 | 1.98 | 23.10 |
| 21 | 40.26 | 2.31 | 18.79 |
| 22 | 7.48 | 1.99 | 5.28 |
| 23 | 7.33 | 1.95 | 2.38 |
| 24 | 7.92 | 2.11 | 6.13 |
| 25 | 5.03 | 6.02 | 4.85 |
| 26 | 6.01 | 1.59 | 8.69 |
| 27 | 7.29 | 1.85 | 19.32 |
| 阳性对照 ^a | 2.67 | 3.72 | 4.12 |

[0099] °印楝乳油(1%印楝素)为拒食活性测试的阳性对照。

[0100] 下述实施例4-12配方中有关组分选择如下：

[0101] 润湿剂可选用：脂肪醇硫酸盐、十二烷基苯磺酸盐、吐温、山梨醇聚氧乙醚、木质素磺酸盐、茶枯、搭皂角；

[0102] 乳化剂可选用：肥皂、烷基苯磺酸钠、脂肪酸聚氧乙烯基酯；

[0103] 稳定剂可选用：环氧植物油、环氧酯；

[0104] 有机溶剂可选用：甲醇、乙醇、丙酮；

[0105] pH值调节剂可选用：醋酸、碳酸氢钠；

[0106] 防腐剂可选用：苯甲酸钠。

[0107] 实施例4：

[0108] 藤状火把花总二萜乳剂拒食剂制备：

[0109] 取实施例1所制得藤状火把花总二萜15g，加入润湿剂20g，乳化剂10g，稳定剂6g，有机溶剂40g，pH值调节剂3g，充分混合搅拌乳化，即得乳剂。

[0110] 实施例5：

[0111] 0.7%二萜拒食剂的制备：

[0112] (A)成分配比(重量)：

[0113] 化合物1含量:0.1%，化合物2含量:0.2%

[0114] 化合物3含量:0.2%，化合物4含量:0.2%

[0115] 润湿剂:20% 乳化剂:20%

[0116] 稳定剂:6% 有机溶剂:53.0%

[0117] pH值调节剂:0.3%

[0118] (B)制备方法:溶液混配法

[0119] 将实施例1所制得化合物1、化合物2、化合物3和化合物4用一定量的溶剂溶解，按配方设定的化合物含量比例混合搅拌，然后加入润湿剂、乳化剂、稳定剂、有机溶剂、pH值调节剂搅拌均匀即可。

[0120] 实施例6:

[0121] 0.8%二萜拒食剂的制备:

[0122] (A)成分配比(重量):

[0123] 化合物1含量:0.2% 化合物7含量:0.4%

[0124] 化合物10含量:0.2% 润湿剂:20%

[0125] 乳化剂:20% 稳定剂:6%

[0126] 有机溶剂:52.9% pH值调节剂:0.3%

[0127] (B)制备方法:溶液混配法

[0128] 将实施例1所制得化合物1、化合物7、化合物10用一定量的溶剂溶解,按配方设定的化合物含量比例混合搅拌,然后加入润湿剂、乳化剂、稳定剂、有机溶剂、pH值调节剂搅拌均匀即可。

[0129] 实施例7:

[0130] 1%二萜拒食剂I的制备:

[0131] (A)成分配比(重量):

[0132] 化合物1含量:0.3% 化合物6含量:0.3%

[0133] 化合物25含量:0.4% 润湿剂:20%

[0134] 乳化剂:20% 稳定剂:6%

[0135] 有机溶剂:52.7% pH值调节剂:0.3%

[0136] (B)制备方法:溶液混配法

[0137] 将实施例1所制得化合物1、化合物6、化合物25用一定量的溶剂溶解,按配方设定的化合物含量比例混合搅拌,然后加入润湿剂、乳化剂、稳定剂、有机溶剂、pH值调节剂搅拌均匀即可。

[0138] 实施例8:

[0139] 1%二萜拒食剂II的制备:

[0140] (A)成分配比(重量):

[0141] 化合物2含量:0.2% 化合物3含量:0.4%

[0142] 化合物17含量:0.4% 润湿剂:20%

[0143] 乳化剂:20% 稳定剂:6%

[0144] 有机溶剂:52.7% pH值调节剂:0.3%

[0145] (B)制备方法:溶液混配法

[0146] 将实施例1所制得化合物2、化合物3、化合物17用一定量的溶剂溶解,按配方设定的化合物含量比例混合搅拌,然后加入润湿剂、乳化剂、稳定剂、有机溶剂、pH值调节剂搅拌均匀即可。

[0147] 实施例9:

[0148] 1%二萜拒食剂III的制备:

[0149] (A)成分配比(重量):

[0150] 化合物3含量:0.2% 化合物8含量:0.4%

[0151] 化合物14含量:0.4% 润湿剂:15%

[0152] 乳化剂:10% 稳定剂:6%

- [0153] 有机溶剂:20% pH值调节剂:0.3%
- [0154] 防腐剂:1% 水:46.7%
- [0155] (B)制备方法:溶液混配法
- [0156] 将实施例1所制得化合物3、化合物8、化合物14用一定量的溶剂溶解,按配方设定的化合物含量比例混合搅拌,然后加入润湿剂、乳化剂、稳定剂、有机溶剂、pH值调节剂、防腐剂和水分搅拌均匀即可。
- [0157] 实施例10:
- [0158] 1.5%二萜拒食剂的制备:
- [0159] (A)成分配比(重量):
- [0160] 化合物1含量:0.4% 化合物2含量:0.5%
- [0161] 化合物4含量:0.6% 润湿剂:15%
- [0162] 乳化剂:10% 稳定剂:6%
- [0163] 有机溶剂:20% pH值调节剂:0.3%
- [0164] 防腐剂:1% 水:46.2%
- [0165] (B)制备方法:溶液混配法
- [0166] 将实施例1所制得化合物1、化合物2、化合物4用一定量的溶剂溶解,按配方设定的化合物含量比例混合搅拌,然后加入润湿剂、乳化剂、稳定剂、有机溶剂、pH值调节剂、防腐剂和水分搅拌均匀即可。
- [0167] 实施例11:
- [0168] 2%二萜拒食剂I的制备:
- [0169] (A)成分配比(重量):
- [0170] 化合物1含量:0.6% 化合物5含量:0.7%
- [0171] 化合物11含量:0.7% 润湿剂:15%
- [0172] 乳化剂:10% 稳定剂:6%
- [0173] 有机溶剂:20% pH值调节剂:0.3%
- [0174] 防腐剂:1% 水:45.7%
- [0175] (B)制备方法:溶液混配法
- [0176] 将实施例1所制得化合物1、化合物5、化合物11用一定量的溶剂溶解,按配方设定的化合物含量比例混合搅拌,然后加入润湿剂、乳化剂、稳定剂、有机溶剂、pH值调节剂、防腐剂和水分搅拌均匀即可。
- [0177] 实施例12:
- [0178] 2%二萜拒食剂II的制备:
- [0179] (A)成分配比(重量):
- [0180] 化合物2含量:0.2% 化合物5含量:0.7%
- [0181] 化合物13含量:1.1% 润湿剂:15%
- [0182] 乳化剂:10% 稳定剂:6%
- [0183] 有机溶剂:20% pH值调节剂:0.3%
- [0184] 防腐剂:1% 水:45.7%
- [0185] (B)制备方法:溶液混配法

[0186] 将实施例1所制得化合物2、化合物5、化合物13用一定量的溶剂溶解,按配方设定的化合物含量比例混合搅拌,然后加入润湿剂、乳化剂、稳定剂、有机溶剂、pH值调节剂、防腐剂和水分搅拌均匀即可。