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# 桑叶中的紫罗兰酮类化合物和脂肪酸类化合物研究

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**摘　要**:对桑叶的化学成分进行分离鉴定。通过硅胶、反相 ODS、Sephadex LH-20 柱色谱和 prep-HPLC 进行分离纯化,从桑叶中分离得到 18 个化合物,运用现代波谱技术分别鉴定为(3*R*)-3-羟基-*β*-紫罗兰酮(**1**)、(6*S*,7*E*,9*S*)-9-hydroxy-megastigma-4,7-dien-3-one(**2**)、dehydro-vomifol(**3**)、(3*S*,9*R*)-3-hydroxy-7,8-didehydro-*β*-ionol 9-*O*-*β*-D-glucopyranoside(**4**)、(6*R*,9*R*)-3-oxo-*α*-ionol 9-*O*-*β*-D-glucopyranoside(**5**)、(*E*)-6-[9-(*β*-D-glucopyranosyloxy)butylidene]-1,1,5-trimethyl-4-cyclohexen-3-one(**6**)、(*Z*)-6-[9-(*β*-D-glucopyranosyloxy) butylidene]-1,1,5-trimethyl-4-cyclohexen-3-one(**7**)、(6*S*,9*S*)-3-*α*-oxo-ionol 9-*O*-*β*-D-glucopyranoside(**8**)、blumenol C 9-*O*-*β*-D-glucopyranoside(**9**)、lcariside B1(**10**)、(3*S*)-*O*-*β*-D-glucopyranosyl-6-[3-oxo-(2*S*)-butenylidenyl]-1,1,5-trimethylcyclohexan-(5*R*)-ol(**11**)、(*E*)-4-((1*S*,3*R*,4*R*)-1-hydroxy-4,5,5-trimethyl-7-oxabicyclo [4.1.0] heptan-1-yl)but-1-en-3-one(**12**)、(6*R*,9*S*)-vomifoliol-9-*O*-*β*-apiofuranosyl-(1′′→6′)-*O*-*β*-glucopy-ranoside(**13**)、(9*R*)-羟基-(10*E*,12*Z*,15*Z*)-十八碳三烯酸(**14**)、(2*E*)-十二碳烯二酸(**15**)、2,5-dihydro-5-oxo-5-furanoctanoic acid(**16**)、1-glyceryl linolenate(**17**)、正三十二烷醇(**18**)。以上化合物均为首次从该植物中分离得到。

**关键词**:桑叶;化学成分;紫罗兰酮类化合物

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# Ionone Derivatives and Fatty Acid from *Morus alba* L. Leaves

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**Abstract**: The chemical constituents of *Morus alab* L. were isolated by column chromatography on silica gel, Rp-18, Sephadex LH-20 and prep-HPLC by chemical and spectral analyses. Eighteen compounds were finally isolated and purified from the leaves of *Morus alab* L.. Their structures were elucidated as (3*R*)-3-hydroxy-*β*-ionone (**1**), (6*S*,7*E*,9*S*)-9-hydroxy-megastigma-4,7-dien-3-one (**2**), dehydrovomifol (**3**), (3*S*,9*R*)-3-hydroxy-7,8-didehydro-*β*-ionol 9-*O*-*β*-D-glucopyranoside (**4**), (6*R*,9*R*)-3-oxo-*α*-ionol 9-*O*-*β*-D-glucopyranoside (**5**), (*E*)-6-[9-(*β*-D-glucopyranosyloxy) butyl-idene]-1,1,5-trimethyl-4-cyclohexen-3-one (**6**), (*Z*)-6-[9-(*β*-D-glucopyranosyloxy) buty-lidene]-1,1,5-trimethyl-4-cyclohexen-3-one (**7**), (6*S*,9*S*)-3-oxo-*β*-ionol 9-*O*-*β*-D-glucopyranoside (8), blumenol C 9-*O*-*β*-D-glucopyranoside (9), lcariside B1 (10), (3*S*)-*O*-*β*-D-glucopy-ranosyl-6-[3-oxo-(2*S*)-butenylidenyl]-1, 1, 5-trimethylcyclohexan-(5*R*)-ol (11), (*E*)-4-((1*S*,3*R*,4*R*)-1-hydroxy-4,5,5-trimethyl-7-oxabicyclo[4.1.0] heptan-1-yl) but-1-en-3-one (**12**), (6*R*,9*S*)-vomifoliol-9-*O*-*β*-apiofuranosyl-(1′′→6′)-*O*-*β*-glucopyranoside (**13**), (9*R*)-hydroxy-(10*E*, 12*Z*, 15*Z*)-octadecatrienoic acid (**14**), (2*E*)-dodecenedioic acid (**15**), 2,5-dihydro-5-oxo-5-furanoctanoic acid (**16**), 1-glyceryl linolenate (**17**), n-dotfiacontanol (**18**). Compounds **1-18** were obtained from this plant or the first time.

**Key words**: *Morus alab* L.; chemical constituents; ioone derivatives

桑叶始载于《神农本草经》,为桑科桑属植物桑 *Morus alba* L. 的干燥叶。本品性寒,味甘苦,具有清肺润燥、清肝明目、疏风散寒的功效[1]。经药理活性筛选发现,桑叶 95% 乙醇提取物具有较强的抗肿瘤活性,对该提取物的氯仿和丙酮部分分离得到 18 个化合物,经波谱分析鉴定为(3*R*)-3-羟基-*β*-紫罗兰酮(**1**),(6*S*,7*E*,9*S*)-9-hydroxy-megastigma-4,7-dien-3-one (**2**), dehydrovomifol (**3**), (3*S*,9*R*)-3-hydroxy-7,8-didehydro-*β*-ionol 9-*O*-*β*-D-glucopyranoside (**4**), (6*R*,9*R*)-3-oxo-*α*-ionol 9-*O*-*β*-D-glucopyranoside (**5**), (*E*)-6-[9-(*β*-D-glucopyranosyloxy) butylidene]-1,1,5-trimethyl-4-cyclohexen-3-one (**6**), (*Z*)-

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6-[9-(β-D-glucopyranosyloxy) butylidene]-1,1,5-trimethyl-4-cyclohexen-3-one (**7**), (6*S*, 9*S*)-3-oxo-β-ionol 9-*O*-β-D-glucopyranoside (**8**), blumenol C 9-*O*-β-D-glucopyranoside (**9**), lcariside B1 (**10**), (3*S*)-*O*-β-D-glucopyranosyl-6-[3-oxo-(2*S*)-butenylidenyl]-1,1,5-trimethylcyclohexan-(5*R*)-ol (**11**), (*E*)-4-((1*S*, 3*R*,4*R*)-1-hydroxy-4,5,5-tri-methyl-7-oxabicyclo[4.1.0] heptan-1-yl) but-1-en-3-one (**12**), (6*R*, 9*S*)-vomifoliol-9-*O*-β-apio-furanosyl-(1′′→6′)-*O*-β-glucopyranoside (**13**), (9*R*)-羟基-(10*E*,12*Z*,15*Z*)-十八碳三烯酸 (**14**), (2*E*)-十二碳烯二酸(**15**), 2,5-dihydro-5-oxo-5-furanoctanoic acid (**16**), 1-glyceryl linolenate (**17**), 正三十二烷醇 (**18**), 化合物 **1** ~ **18** 均为首次从该植物中分离得到。

## 1 仪器与材料

熔点用 Boetius 显微熔点测定仪(温度未校正)测定;旋光用 Jasco P2000 型旋光仪测定;CD 谱用 JASCO J-815 圆二色谱仪测定;核磁共振谱用美国 Varian 公司 Mercury-300 型, Mercury-400 型和 INOVA-500 型核磁共振波谱仪测定, TMS 为内标; ESI-MS 用 Agilent 1100 LC/MSD Trap SL 型液相色谱质谱连用仪测定。Sephadex LH-20 为 Pharmacia 公司产品; Rp-$C_{18}$ (50 um) 为 YMC 公司产品。柱色谱和薄层色谱硅胶均为青岛海洋化工厂产品。溶剂均为分析纯,为北京化工厂产品。

桑叶于 2011 年 7 月采于北京国森公司桑园,经中国医学科学院药物研究所马林副教授鉴定为桑科桑属植物(*Morus alab* L.)的叶,标本(NO. ID-S-2543)存放于中国医学科学院药物研究所标本室。

## 2 提取与分离

桑叶 30 kg 粉碎后用 95% 乙醇回流提取 3 次,每次 1 h,合并提取液,减压浓缩得浸膏 2.9 kg。浸膏用 5 kg 硅胶(160 ~ 200 目)拌样,依次用石油醚、氯仿、乙酸乙酯、丙酮和甲醇进行快速洗脱,减压浓缩得石油醚部分 793 g、氯仿部分 355 g、乙酸乙酯部分 360 g、丙酮部分 423 g、甲醇部分 900 g。

氯仿部分 355 g 用 1 Kg 硅胶(160 ~ 200 目)拌样经硅胶柱色谱分离,以石油醚-丙酮(100∶0 ~ 0∶100)梯度洗脱,得到 7 个部分 Fr. 1 ~ Fr. 7。Fr. 3 (120 g)经反复硅胶柱色谱(石油醚-丙酮洗脱)、Rp-18 和 Sephadex LH-20 分离,得到化合物 18 (10 mg);Fr. 4 (80 g)经反复硅胶柱色谱(石油醚-丙酮洗脱)、RP-18 和 Sephadex LH-20 分离,得到化合物 **1** (25 mg);Fr. 5 (35 g)经反复硅胶柱色谱(石油醚-丙酮洗脱)、RP-18 和 Sephadex LH-20 分离,得到化合物 **2** (57 mg),化合物 **3** (28 mg),化合物 **12** (23 mg),化合物 **14** (45 mg);Fr. 6 (20 g)经反复硅胶柱色谱(石油醚-丙酮洗脱)、RP-18 和 Sephadex LH-20 分离,得到化合物 **15** (20 mg),化合物 **16** (23 mg),化合物 **17** (14 mg)。

丙酮部分 423 g 上大孔树脂柱分离,以乙醇-水(0∶10、3∶7、6∶4、10∶0)洗脱,收集各部分后分别浓缩。30 % 乙醇部分(120 g)进行反复硅胶柱色谱(氯仿-甲醇洗脱)、RP-18 和 Sephadex LH-20 分离,得到化合物 **4** (53 mg),化合物 **5** (45 mg),化合物 **6** (26 mg),化合物 **7** (26 mg),化合物 **8** (128 mg),化合物 **9** (100 mg),化合物 **10** (94 mg),化合物 **11** (20 mg),化合物 **13** (8 mg)。

## 3 结构鉴定

**化合物 1** 淡黄色油状物,[α]-44.3° (0.30, $CHCl_3$);ESIMS *m/z*:209 $[M-H]^-$,分子式为 $C_{13}H_{20}O_2$;$^1$H NMR (300 MHz, DMSO):δ 7.17 (1H, d, *J* = 16.5 Hz, H-7), 6.01 (1H, d, *J* = 16.5 Hz, H-8), 3.72 (1H, m, H-3), 2.27 (1H, dd, *J* = 17.4, 5.4 Hz, H-4e), 1.93 (1H, dd, *J* = 17.4, 9.3 Hz, H-4a), 1.64 (1H, m, H-2e), 1.30 (1H, t, *J* = 12 Hz, H-2a), 2.22 (3H, s, H-10), 1.71 (3H, s, $CH_3$-13), 1.05, 1.02 (3H × 2, s, $CH_3$-11,12),以上数据与文献[2]报道的数据一致,故将该化合物鉴定为(3*R*)-3-羟基-β-紫罗兰酮。

**化合物 2** 淡黄色油状物,[α]-94.8 (*c* 0.16, MeOH);ESIMS *m/z*:231.42 $[M+Na]^+$;$^1$H NMR (DMSO-$d_6$, 500 MHz) δ:5.80 (1H, s, H-4), 5.60 (1H, dd, *J* = 15.5, 6.0 Hz, H-8), 5.47 (1H, dd, *J* = 15.5, 9.0 Hz, H-7), 4.14 (1H, m, H-9), 2.57 (1H, *J* = 9.5 Hz, H-6), 2.31 (1H, d, *J* = 16.5 Hz, H-2a), 1.93 (1H, d, *J* = 16.5 Hz, H-2b), 1.87 (3H, s, H-13), 1.11 (3H, d, *J* = 6.5 Hz, H-10), 0.94 (3H, s), 0.88 (3H, s);$^{13}$C NMR (DMSO-$d_6$, 125MHz) δ: 198.0 (C-3), 162.5 (C-5), 139.6 (C-8), 125.0 (C-4), 124.8 (C-7), 66.4 (C-9), 54.6 (C-6), 47.2 (C-2), 35.8 (C-1), 27.5 (C-10), 26.8 (C-13), 24.1 (C-11), 23.1 (C-12)。以上数据与文献[3]报

道的数据一致,故将该化合物鉴定为(6*S*,7*E*,9*S*)-9-hydroxy-megastigma-4,7-dien-3-one。

**化合物 3** 白色无定形固体;[α] +158.0° (0.13, MeOH);ESIMS, *m/z* 245.3 [M + Na]$^+$. $^1$HNMR (DMSO-$d_6$,300 MHz) δ:6.45 (1H,d,*J* = 15.6 Hz,H-7),5.75 (1H,d,*J* = 15.6 Hz,H-8),5.34 (1H,s,H-4),4.87 (1H,OH),2.11 (1H,d,*J* = 17.1 Hz,H-2a),1.64 (1H,d,*J* = 17.1 Hz,H-2e),1.74 (3H,s,H-10),1.28 (3H,d, *J* = 6.5 Hz,H-13),0.44 (3H,s,H-11),0.40 (3H,s,H-12);$^{13}$CNMR (DMSO-$d_6$,125MHz) δ:198.3 (C-1 or 9),197.1 (C-9 or 1),161.7 (C-5),147.2 (C-7),130.6 (C-8),126.6 (C-4),78.2 (C-6),49.3 (C-2),41.2 (C-1),27.3 (C-10),24.3 (C-12),23.2 (C-11),18.6 (C-13). 以上数据与文献[4]报道的数据一致,故将该化合物鉴定为 dehydrovomifol。

**化合物 4** 淡黄色胶状物;[α]-17.7° (0.18 MeOH);ESIMS, *m/z* 393.2 [M + Na]$^+$, $^1$H NMR (DMSO-$d_6$,300 MHz) δ:1.67 (1H,dd,*J* = 17.5, 1.0 Hz,H-2a),1.24 (1H,dd, *J* = 17.5,5.5 Hz,H-2b),3.70 (1H,m,H-3),2.23 (1H,dd,*J* = 17.5, 5.0 Hz,H-4a),1.69 (1H,dd, *J* = 17.5,9.5 Hz,H-4b),4.76 (1H,quart,*J* = 6.5 Hz,H-9),1.40 (3H, d,*J* = 6.5 Hz,H-10),1.03 (3H,s,H-11),1.08 (3H,s,H-12),1.80 (3H,s,H-13),1.51 (2H,m,H-3),4.36 (1H,d,*J* = 8.0 Hz,H-1′),3.0-3.7 (6H, m, H-2′-6′);$^{13}$ C NMR (DMSO-$d_6$, 125MHz) δ: 138.22 (C-5),122.5 (C-6),100.57 (C-1′),93.5 (C-8),82.6 (C-7),77.0 (C-5′),76.8 (C-3′),73.6 (C-2′),69.8 (C-4′),64.3 (C-9),62.5 (C-3),60.8 (C-6′),46.4 (C-2),39.9 (C-4),35.9 (C-1),30.3 (1-$CH_3$),28.4 ($CH_3$-1),22.3 (C-10),22.1 ($CH_3$-5)。以上数据与文献[5]报道的数据一致,故将该化合物鉴定为(3*S*,9*R*)-3-hydroxy-7,8-didehydro-β-ionol 9-*O*-β-D-glucopyranoside。

**化合物 5** 淡黄色油状物;[α] +355 (0.39, MeOH),ECD (MeOH) 245 (Δε +21.1) nm,316 (Δε-1.2) nm;ESIMS, *m/z* 393.3 [M + Na]$^+$,$^1$H NMR (DMSO-$d_6$, 300 MHz) δ:1.96 (1H,d,*J* = 16.5 Hz,H-2a),2.33 (1H,d, *J* = 16.5 Hz,H-2β), 5.81 (1H,br s,H-4),2.61 (1H,d, *J* = 8.7 Hz,H-6),5.58 (1H,d,*J* = 15.6,8.7 Hz,H-7),5.68 (1H,dd,*J* = 15.6,6.3 Hz,H-8),4.28 (1H,m,H-9),1.19 (3H,d,*J* = 6.3 Hz,H-10),0.95 (3H,s, H-11),0.91 (3H,s,H-12),1.86 (3H,s,H-13), 4.18 (1H,d,*J* = 7.8 Hz,H-1′),2.9-3.1 (4H,m,H-2′-4′),3.44 (1H,d,*J* = 11.7,6.0 Hz,H-6′a),3.61 (1H,d, *J* = 11.7,2.0 Hz,H-6′b);$^{13}$C NMR (DMSO-$d_6$, 125 MHz) δ:162.0 (C-5),54.6 (C-6), 100.9 (C-1′),136.7 (C-8),127.3 (C-7),76.8 (C-5′),76.8 (C-3′),73.7 (C-2′),69.9 (C-4′),74.7 (C-9),197.9 (C-3),60.9 (C-6′),47.1 (C-2), 124.9 (C-4),35.6 (C-1),26.7 (C-11),27.4 (C-12),20.8 (C-10),22.1 (C-13). 以上数据与文献[6]报道的数据一致,故将该化合物鉴定为(6*R*, 9*R*)-3-oxo-α-ionol 9-*O*-β-D-glucopyranoside。

**化合物 6** 淡黄色油状物;ESIMS, *m/z* 393.3 [M + Na]$^+$. $^1$H NMR (DMSO-$d_6$,300 MHz) δ:6.19 (1H,t,*J* = 6.5 Hz,H-7),5.82 (1H,br. s,H-4), 4.19 (1H,d,*J* = 7.5 Hz,H-1′),3.89 (1H,m,H-9),3.64 (1H,dd,*J* = 14.5,3.5 Hz,H-6′a),3.41 (1H,dd,*J* = 14.5,6.0 Hz,H-6′b),3.11 (2H,m,H-3′,5′),3.04 (1H,m,H-4′),2.92 (1H,m,H-2′), 2.58 (2H,t,*J* = 6.5 Hz,H-8),2.25 (2H,br. s, H-2),2.04 (3H,s,H-13),1.22 (3H,s,H-11 or 12), 1.20 (3H,s,H-12 or 11),1.17 (3H,d,*J* = 6.5 Hz, H-10);$^{13}$C NMR (DMSO-$d_6$,125 MHz) δ:197.9 (C-3),155.4 (C-5),141.3 (C-6),133.2 (C-7),124.5 (C-4),101.1 (C-1′),76.8 (C-3′),76.8 (C-5′), 73.7 (C-9),73.4 (C-2′),70.3 (C-4′),61.4 (C-6′),53.3 (C-2),37.7 (C-8),36.9 (C-1),28.5, 28.3 (C-11,12),21.8 (C-13),19.9 (C-10). 以上数据与文献[7]报道的数据一致,故将该化合物鉴定为(*E*)-6-[9-(β-D-glucopyranosyloxy) butylidene]-1, 1,5-trimethyl-4-cyclohexen-3-one。

**化合物 7** 淡黄色油状物;ESIMS, *m/z* 393.3 [M + Na]$^+$,$^{13}$ C NMR (DMSO-$d_6$, 125 MHz):δ 197.7 (C-3),155.8 (C-5),142.6 (C-6),128.4 (C-7),127.8 (C-4),101.1 (C-1′),76.8 (C-3′),76.8 (C-5′),73.7 (C-9),73.5 (C-2′),70.4 (C-4′), 61.4 (C-6′),52.3 (C-2),40.3 (C-1),37.2 (C-8), 27.8 ($CH_3$),27.7 ($CH_3$),24.2 ($CH_3$) and 19.7 (C-10). 以上数据与文献[7]报道的数据一致,故将该化合物鉴定为(*Z*)-6-[9-(β-D-glucopyranosyloxy) butylidene]-1,1,5-trimethyl-4-cyclohexen-3-one。

**化合物 8** 无色油状物,[α]-134.2 (0.15,

MeOH);ECD (MeOH) 246 ($\Delta\varepsilon$-24.1) nm,315 ($\Delta\varepsilon$ +1.2) nm;ESIMS,*m/z* 393.3 [M + Na]$^+$. $^1$H NMR ($CD_3Cl$,500 MHz) δ:2.06 (1H,d,*J* = 16.5 Hz,H-2a),2.34 (1H,d, *J* = 16.5 Hz,H-2$\beta$),5.91 (1H, br s,H-4),2.54 (1H,d, *J* = 8.5 Hz,H-6),5.58 (1H,d,*J* = 15.0,8.5 Hz,H-7),5.68 (1H,dd,*J* = 15.0,6.5 Hz,H-8),4.31 (1H,m,H-9),1.31 (3H, d,*J* = 6.0 Hz, H-10),0.96 (3H,s,H-11),1.03 (3H,s,H-12),1.91 (3H,d,*J* = 0.5 Hz,H-13), 4.35 (1H,d,*J* = 7.5 Hz,H-1′),3.2-3.8 (6H,m,H-2′-6′);$^{13}$C NMR ($CD_3Cl$,125MHz) δ:162.3 (C-5), 55.4 (C-6),101.6 (C-1′),136.5 (C-8),128.2 (C-7),76.5 (C-5′),77.3 (C-3′),73.7 (C-2′),69.9 (C-4′),75.7 (C-9),199.5 (C-3),61.8 (C-6′), 47.5 (C-2),125.9 (C-4),36.3 (C-1),26.9 (C-11),27.4 (C-12),21.5 (C-10),23.8 (C-13). 以上数据与文献[6]报道的数据一致,故将该化合物鉴定为(6*S*,9*S*)-3-oxo-α-ionol 9-*O*-$\beta$-D-glucopyranoside。

**化合物 9** 无色油状物;[α] +25.8 (0.24, MeOH);ESIMS,*m/z* 395.3 [M + Na]$^+$;$^{13}$C NMR (DMSO-$d_6$,125MHz) δ:166.0 (C-5),50.1 (C-6), 100.7 (C-1′),36.2 (C-8),25.0 (C-7),76.8 (C-5′),76.9 (C-3′),73.2 (C-2′),70.3 (C-4′),73.5 (C-9),198.0 (C-3),61.3 (C-6′),47.0 (C-2), 124.2 (C-4),36.0 (C-1),26.7 (C-11),28.5 (C-12),19.5 (C-10),24.1 (C-13). 以上数据与文献[8]报道的数据一致,故将该化合物鉴定为 blumenol C 9-*O*-$\beta$-D-glucopyranoside。

**化合物 10** 白色粉末;[α]-61.1 (0.25, MeOH);ESIMS,*m/z* 409.2 [M + Na]$^+$. $^1$H NMR (DMSO-$d_6$,400 MHz) δ:5.76 (1H,s,H-8),4.24 (1H,d,*J* = 7.6 Hz,H-1′),4.17 (1H,m,H-3),3.67 (1H,br. d, *J* = 11.6Hz,H-6′a),3.45 (1H,dd,*J* = 11.6,5.2 Hz,H-6′b),2.86-3.17 (4H,m,Glc-H), 2.25 (1H,dd,*J* = 12.8,1.6 Hz,H-4eq),1.98 (1H, dd,*J* = 12.8,2.4 Hz,H-2eq),1.30 (2H,overlapped, H-2ax,4ax,),2.11 (3H,s,H-10),1.32 (3H,s,H-13),1.28 (3H,s,H-12),1.07 (3H,s,H-11);$^{13}$C NMR (DMSO-$d_6$,125MHz) δ:209.1 (C-7),197.8 (C-9),118.6 (C-6),101.4 (C-1′),99.6 (C-8), 76.8 (C-3′),76.7 (C-5′),73.5 (C-2′),70.7 (C-3),70.4 (C-5),70.1 (C-4′),61.0 (C-6′),47.0 (C-2),46.1 (C-4),35.5 (C-1),31.6 (C-11),30.3 (C-13),28.7 (C-12),26.1 (C-10). 以上数据与文献[9]报道的数据一致,故将该化合物鉴定为 Icariside $B_1$。

**化合物 11** 白色粉末;[α]-6.72° (0.22, MeOH);ESIMS,*m/z* 409.2 [M + Na]$^+$. $^1$HNMR (DMSO-$d_6$,400 MHz) δ:5.84 (1H,s,H-8),4.23 (1H,d,*J* = 7.6 Hz,H-1′),4.16 (1H,m,H-3),3.67 (1H,dd,*J* = 11.6,5.2,1.2 Hz,H-6′a),3.45 (1H, quint,*J* = 6.0 Hz,H-6′b),2.86-3.17 (4H,m,Glc-H),2.21 (1H,overlapped,H-4eq),1.97 (1H,dd,*J* = 12.4,2.4 Hz,H-2eq),1.23 (2H,overlapped,H-2ax,4ax,),2.21 (3H,s,H-10),1.37 (3H,s,H-12),1.27 (3H,s,H-13),1.05 (3H,s,H-11);$^{13}$C NMR (DMSO-$d_6$,125MHz) δ:208.9 (C-7),198.8 (C-9),118.4 (C-6),101.6 (C-1′),99.9 (C-8), 76.7 (C-3′),76.7 (C-5′),73.4 (C-2′),70.9 (C-3),70.5 (C-5),70.1 (C-4′),61.1 (C-6′),46.9 (C-2),46.1 (C-4),35.4 (C-1),31.8 (C-11),30.3 (C-13),28.6 (C-12),26.7 (C-10). 以上数据与文献[9]报道的数据一致,故将该化合物鉴定为(3*S*)-*O*-$\beta$-D-glucopyranosYL-6-[ 3-oxo-( 2*S* )-butenylidenyl]-1,1,5-trimethylcyclo hexan-(5*R*)-ol。

**化合物 12** 白色粉末;[α]-84.5 (0.34, MeOH);$^1$H NMR (DMSO-$d_6$, 400 MHz) δ:7.07 (1H,d,*J* = 20.8 Hz,H-7),6.00 (1H,d,*J* = 20.8 Hz,H-8),3.60 (1H,m,H-3),2.17 (1H,dd,*J* = 18.1,6.0 Hz,H-2a),1.55 (1H,dd,*J* = 18.1,11.6 Hz,H-2b),1.45 (3H,dd, *J* = 16.0,2.0 Hz,H-4a), 1.18 (3H,dd, *J* = 16.0,1.2 Hz,H-4b),2.23 (3H, s,H-10),1.11 (3H,s,H-13),1.13 (3H,s,H-12), 1.13 (3H,s,H-11);$^{13}$C NMR (DMSO-$d_6$,150 MHz) δ:197.4 (C-9),143.4 (C-7),132.2 (C-8),68.8 (C-6),66.9 (C-5),61.8 (C-3),46.5 (C-2),40.4 (C-4),34.5 (C-1),29.0,24.8 (C-11,12),27.3 (C-10),19.7 (C-13). 以上数据与文献[10]报道的数据一致,故将该化合物鉴定为(*E*)-4-((1*S*,3*R*,4*R*)-1-hydroxy-4,5,5-trimethyl-7-oxabicyclo[4.1.0] heptan-1-yl) but-1-en-3-one:

**化合物 13** 白色粉末;[α]-5.5° (0.54, MeOH);$^{13}$C NMR (DMSO-$d_6$,125MHz) δ:152.6 (C-3,5),147.5 (C-3′),145.9 (C-4′),137.2 (C-4), 133.7 (C-1),132.2 (C-1′),118.7 (C-6′),115.1 (C-5′),102.7 (C-1″),85.1 (C-7,7′),77.2 (C-

5″), 76.5 (C-3″), 74.1 (C-2″), 71.2 (C-9′), 71.1 (C-9), 69.9 (C-4″), 60.9 (C-6″), 56.4, (3, 5-OMe), 56.0 (3′-OMe), 53.7 (C-8′), 53.5 (C-8), 以上数据与文献[11]报道的数据一致,故将该化合物鉴定为 Eucommin A。

**化合物 14** 淡黄色无定形固体;[α]-3.04° (0.58 $CHCl_3$);ESIMS *m/z* 317.2 $[M+Na]^+$, $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ:2.18 (2H, t, 9.6), 1.47 (2H, m, H-3), 1.38 (2H, m, H-8), 2.04 (2H, m, H-17), 0.92 (3H, t, *J* = 9.6 Hz, H-18), 3.97 (1H, m, H-9), 5.66 (1H, dd, *J* = 15.5, 6.0 Hz, H-10), 6.44 (1H, dd, *J* = 15.5, 11.5 Hz, H-11), 5.26-5.40 (3H, m, H-12, 15, 16), 5.96 (1H, t, *J* = 11.0 Hz, H-13), 2.88 (2H, dd, *J* = 11.0, 7.5, Hz, H-14), 1.24 (6H, m, H-4-6); $^{13}C$ NMR (DMSO-$d_6$, 125 MHz) δ:174.5 (C-1), 138.6 (C-10), 131.7 (C-16), 128.7 (C-13), 128.3 (C-12), 126.7 (C-15), 123.5 (C-11), 70.44 (C-9), 37.2 (C-8), 33.7 (C-2), 28.5, 28.8, 28.9 (C-4-6), 25.5 (C-14), 24.9 (C-7), 24.5 (C-3), 20.0 (C-17), 14.1 (C-18). 以上数据与文献[12]报道的数据一致,故将该化合物鉴定为(9*R*)-羟基-(10*E*,12*Z*,15*Z*)-十八碳三烯酸

**化合物 15** 白色粉末;ESIMS, *m/z* 251.3 $[M+Na]^+$, $^1H$ NMR (DMSO-$d_6$, 300 MHz) δ:6.79 (1H, m, H-3), 5.75 (1H, d, *J* = 15.5 Hz, H-2), 2.16 (4H, m, H-4, 11), 1.39 (2H, m, H-5), 1.25 (8H, m, H-6-9), 1.50 (2H, m, H-10); $^{13}C$ NMR (DMSO-$d_6$, 125MHz) δ:167.3 (C-1), 122.2 (C-2), 148.7 (C-3), 31.5 (C-4), 27.6 (C-5), 28.6, 28.7 (C-6-9), 24.6 (C-10), 33.8 (C-11), 174.6 (C-12). 以上数据与文献[13]报道的数据一致,故将该化合物鉴定为(2*E*)-十二碳烯二酸。

**化合物 16** 淡黄色油状物,[α] + 5.9° (0.08, MeOH);ESIMS, *m/z* 249.1 $[M+Na]^+$. $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ:7.83 (1H, d, *J* = 5.0 Hz, H-4), 6.20 (1H, dd, *J* = 5.0, 2.0 Hz, H-3), 5.14 (1H, t, *J* = 5.5, H-5), 1.71 (1H, m, H-6a), 1.55 (1H, m, H-6b), 1.47 (2H, m, H-7), 2.18 (2H, t, *J* = 7.0 Hz, H-12), 1.31 (8H, m, H-8-11); $^{13}C$ NMR (DMSO-$d_6$, 125 MHz) δ:174.6 (C-13), 173.1 (C-2), 158.8 (C-4), 120.3 (C-3), 83.2 (C-5), 33.8 (C-12), 32.5 (C-6), 28.7, 28.6, 28.5 (C-8, 9, 10), 24.6 (C-7), 24.2 (C-11), 以上数据与文献[14]报道的数据一致,故将该化合物鉴定为 2,5-Dihydro-5-oxo-5-furanoctanoic acid。

**化合物 17** 淡黄色油状物;ESIMS, *m/z* 375.5 $[M+Na]^+$, $^1H$ NMR (DMSO-$d_6$, 500 MHz) δ:2.28 (2H, t, *J* = 7.5 Hz, H-2), 2.02 (2H, m, H-8), 2.77 (2H, t, *J* = 6.0, H-11), 2.03 (2H, m, H-17), 0.92 (3H, t, *J* = 7.5, H-18), 5.3 (6H, m, H-9, 10, 12, 13, 15, 16), 1.51 (2H, m, H-3), 1.26 (10H, m, H-4-7), 4.03 (1H, dd, *J* = 11.5, 4.5, H-1′a), 3.89 (1H, dd, *J* = 11.5, 7.0, H-1′b), 3.62 (2H, m, H-2′), 3.3 (H-3′, overlapped); $^{13}C$ NMR (DMSO-$d_6$, 125MHz) δ:173.0 (C-1), 33.6 (C-2), 24.5 (C-3), 28.6, 28.6, 28.7, 29.0, (C-4, 5, 6, 7), 26.6 (C-8), 25.2, 25.3 (C-11, 14), 130.0 (C-9), 131.6 (C-16), 127.1, 127.6, 128.0, 128.0 (C-10, 12, 13, 15), 20.1 (C-17), 14.2 (C-18), 65.6 (C-1′), 69.4 (C-2′), 62.7 (C-3′). 以上数据与文献[15]报道的数据一致,故将该化合物鉴定为 1-α Glyceryl linolenate。

**化合物 18** 白色无定形固体;ESIMS *m/z*: 465.2 $[M-H]^-$; $^1H$ NMR ($CDCl_3$, 300 MHz):δ 3.64 (2H, t, *J* = 6.6 Hz, H-1), 1.25 (60H, br s, CH2 (30), 0.88 (3H, t, *J* = 6.0 Hz, H-32); $^{13}C$ NMR ($CDCl_3$, 150 MHz):δ 63.2 (C-1), 33.0 (C-2), 32.0 (C-3), 29.8 (C-4-26), 29.7 (C-27), 29.5 (C-28), 29.4 (C-29), 25.8 (C-30), 22.8 (C-31), 14.1 (C-32). 以上数据与文献[16]报道的数据一致,故将该化合物鉴定为正三十二烷醇。

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