紫丁香籽化学成分研究

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摘　要：目的　研究紫丁香 *Syringa oblata* 籽醋酸乙酯提取物和正丁醇提取物的化学成分。**方法**　采用硅胶柱色谱和高效液相色谱等进行分离纯化，通过薄层色谱及波谱数据进行结构鉴定。**结果**　分离得到了 14 个单体化合物，分别鉴定为丁香苦素 C（**1**）、丁香苦素 A（**2**）、丁香苦素 B（**3**）、(8*E*)-女贞子苷（**4**）、(8*E*)-女贞苷（**5**）、丁香苦苷（**6**）、syringopicroside B（**7**）、4-*O*-11-methyloleoside-*p*-hydroxyphenyl-(6′-11-methyloleoside)-β-*D*-glucopyranoside（**8**）、7β-*D*-glucopyranosyl-11-methyloleoside（**9**）、lilacoside（**10**）、对羟基苯乙醇（**11**）、2-(*p*-hydroxyphenyl)-ethyl-2, 6-bis (2*S*, 3*E*, 4*S*)-3-ethylidene-2-(β-*D*-glucopyranosyloxy)-3, 4-dihydro-5-(methoxycarbonyl)-2H-pyran-4-acetate（**12**）、对羟基苯乙醇丙酸酯（**13**）、21α-hydroxy-serrat-14-en-3β-yl-dihydrocaffeate（**14**）。**结论**　化合物 **1** 为新化合物，化合物 **8**、**12**、**14** 首次从该植物中分离得到。

关键词：紫丁香；丁香苦素 C；丁香苦苷；对羟基苯乙醇丙酸酯；21α-hydroxy-serrat-14-en-3β-yl-dihydrocaffeate
中图分类号：R284.1　　**文献标志码：**A　　**文章编号：**0253 - 2670(2011)10 - 1894 - 06

Chemical constituents from seeds of *Syringa oblata*

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Abstract: Objective　To study the chemical constituents in ethyl acetate and butanol fractions from seeds of *Syringa oblata*. **Methods** The compounds were isolated by silica gel column chromatography and HPLC, and their structures were elucidated by means of spectral analyses. **Results**　Fourteen compounds were identified as syringopicrogenin C (**1**), syringopicrogenin A (**2**), syringopicrogenin B (**3**), (8*E*)-nüzhenlde (**4**), (8*E*)-ligstroside (**5**), syringopicroside (**6**), syringopicroside B (**7**), 4-*O*-11-methyl-oleoside-*p*-hydroxyphenyl-(6′-11-methyloleoside)-β-*D*-glucopyranoside (**8**), 7β-*D*-glucopyranosyl-11-methyloleoside (**9**), lilacoside (**10**), *p*-hydroxyphenylethanol (**11**), 2-(*p*-hydroxyphenyl)-ethyl-2, 6-bis (2*S*, 3*E*, 4*S*)-3-ethylidene-2-(β-*D*-glucopyranosyloxy)-3, 4-dihydro-5-(methoxycarbonyl)-2H-pyran-4-acetate (**12**), *p*-hydroxyphenylethyl propyl ester (**13**), and 21α-hydroxy-serrat-14-en-3β-yl-dihydrocaffeate (**14**). **Conclusion**　Compound **1** is a new one. Compounds **8**, **12**, and **14** are isolated from the seeds of *S. oblata* for the first time.

Key words: *Syringa oblata* Lindl.; syringopicrogenin C; syringopicroside; *p*-hydroxyphenylethanol; 21α-hydroxy-serrat-14-en-3β-yl-dihydrocaffeate

木犀科丁香属植物紫丁香 *Syringa oblata* Lindl. 是常用温里药，具有抗菌消炎、保肝、利胆等功效，用于治疗脾胃湿寒、心腹冷痛、风湿痛、肾虚等，临床应用广泛。研究表明，紫丁香叶、树皮以及种子外壳的化学成分主要为环烯醚萜及其苷类、苯乙醇类等[1-5]。为进一步开发利用紫丁香植物资源，本实验对紫丁香籽的化学成分进行了研究，从中分离鉴定了 14 个单体化合物，其中一个为新化合物，命名为丁香苦素 C（syringopicrogenin C，**1**），其他 13 个化合物分别鉴定为丁香苦素 A（syringopicrogenin A，**2**）、丁香苦素 B（syringopicrogenin B，**3**）、(8*E*)-女贞子苷[(8*E*)-nüzhenlde，**4**]、(8*E*)-女贞苷[(8*E*)-ligstroside，**5**]、丁香苦苷（syringopicroside，**6**）、syringopicroside B（**7**）、4-*O*-11-methyloleoside-*p*-hydroxyphenyl-(6′-11-methyloleoside)-β-*D*-glucopyranoside（**8**）、7β-*D*-glucopyranosyl-11-methyloleoside（**9**）、lilacoside（**10**）、对羟基苯乙醇（*p*-hydroxyphenylethanol，**11**）、2-(*p*-hydroxyphenyl)-ethyl-2, 6-bis (2*S*, 3*E*, 4*S*)-3-ethylidene-2-(β-*D*-glucopyranosyloxy)-3, 4-dihydro-5-(methoxy-

收稿日期：2011-03-19
基金项目：教育部留学回国基金项目（2005383）
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网络出版时间：2011-09-20　　网络出版地址：http://www.cnki.net/kcms/detail/12.1108.R.20110920.1608.002.html

carbonyl)-2H-pyran-4-acetate（**12**）、对羟基苯乙醇丙酸酯（*p*-hydroxyphenylethyl propyl ester，**13**）、21α-hydroxy-serrat-14-en-3β-yl-dihydrocaffeate（**14**）。化合物 **8**、**12**、**14** 为首次从该植物中分离得到。

1 材料与仪器

北京泰克仪器有限公司 X—6 显微熔点测定仪；美国 Nicolet 公司 Magna FTIR—750 型傅里叶变换红外光谱仪；日本电子制 Jeol Gcmate Bu—20 型质谱仪；Bruker AM—400 型核磁共振波谱仪（TMS 为内标）；高效液相色谱仪：Hitachi L—7100，GL Scirnces Inc. Inertsil Prep-ODS（10 nm×250 mm）不锈钢柱；青岛海洋化工厂产柱色谱用硅胶（200～300 目），薄层色谱硅胶板为烟台化工厂产品，其他有机溶剂为国药集团上海试剂厂产品。

紫丁香籽于 2006 年 9 月 24 日采于齐齐哈尔大学校园内，经本校植物学教授沙伟鉴定为 *Syringa oblata* Lindl.的种子。

2 提取与分离

将去壳并晒干的紫丁香籽 1.5 kg，粉碎后室温下每次用 5.0 L 95%乙醇浸泡 3 d 后滤过，重复提取 3 次，合并提取液，浓缩至约 200 mL，加入等量的水混悬，依次用正己烷、醋酸乙酯和正丁醇萃取 3 次，分别合并不同溶剂的萃取液，浓缩得正己烷萃取物 47.3 g，醋酸乙酯萃取物 27.7 g，正丁醇萃取物 61.2 g。

取醋酸乙酯萃取物 10.0 g，用硅胶柱色谱分离，依次用醋酸乙酯、醋酸乙酯-甲醇混合溶剂、甲醇梯度洗脱，得 6 个组分，将各部分经多次硅胶柱色谱和高效液相色谱进一步分离纯化得化合物 **1**（6.4 mg）、**2**（7.2 mg）、**3**（10.9 mg）、**4**（3.5 g）、**5**（562.3 mg）、**6**（627.2 mg）、**7**（15.1 mg）、**8**（412.6 mg）、**9**（8.3 mg）、**10**（13.3 mg）、**11**（5.1 mg）、**12**（9.1 mg）。取正丁醇萃取物 15.8 g，用硅胶柱色谱分离，依次用醋酸乙酯-甲醇混合溶剂、甲醇梯度洗脱，得 5 个组分，各部分经多次硅胶柱色谱和高效液相色谱进一步分离纯化得化合物 **4**（6.5 g）、**5**（34.6 mg）、**6**（18.5 mg）、**8**（900.3 mg）、**13**（583.2 mg）、**14**（7.5 mg）。

3 结构鉴定

化合物 **1**：白色针晶（EtOAc）；mp 156.0～158.5 ℃；HR-ESI-MS *m/z*: 364.151 8，给出分子式 $C_{19}H_{24}O_7$（理论值 364.152 2）；$[\alpha]_D^{24}$ –43.0°（*c* 0.25，MeOH）；红外光谱给出羟基（3 388 cm^{-1}），五元环酮羰基（1 720 cm^{-1}），酯羰基（1 706 cm^{-1}）及苯环（1 519，1 448 cm^{-1}）的吸收；^{1}H-NMR（DMSO-d_6，400 MHz）在 δ 9.19（1H, s）给出一个可能为酚羟基的质子，δ 7.01（2H, d, J = 8.8 Hz）和 6.66（2H, d, J = 8.8 Hz）处给出 1 个对取代苯 AA′BB′系统质子的吸收信号，在 δ 6.71（1H, d, J = 4.4 Hz），5.18（1H, d, J = 4.4 Hz）和 4.96（1H, d, J = 8.8 Hz）处各给出 1 个双峰的质子，在 δ 3.27（3H, s）处给出 1 个甲氧基，在 δ 0.99（3H, d, J = 6.9 Hz）处给出 1 个双峰的甲基；^{13}C-NMR（DMSO-d_6, 100 MHz）谱给出 19 个碳，其中 δ 217.3 为一酮羰基碳，δ 171.8 为一酯羰基碳，δ 98.0 和 92.0 可能为两个缩醛（或半缩醛）碳的吸收信号；DEPT 给出两个甲基，3 个亚甲基，10 个次甲基和 4 个季碳；HMBC 中 H-5 与 C-1、C-3、C-4、C-6、C-7、C-8、C-9、C-11 相关，H-10 与 C-7、C-9 相关，H-α 与 C-11 相关。该结果与丁香苦素 A 基本一致[5]，又由 HMBC 中 H-OCH_3 与 C-3 相关，H-3 与 C-1、C-11 相关，H-4 与 C-3、C-5、C-6、C-11 相关，推得甲氧基连在 3 位，进而确定化合物 **1** 的平面结构为 3-甲氧基环烯醚萜酸对羟基苯乙醇酯（图 1）。

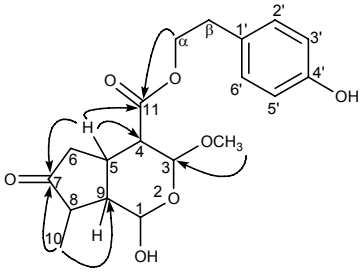

图 1 化合物 1 的结构及主要的 HMBC 相关

Fig. 1 Structure and key HMBC correlations of compound 1

由 NOESY（图 2）可知，H-3 与 H-5 相关，H-8 与 H-1、H-9 相关，H-9 与 H-5、H-6β、H-8 相关，H-4（δ 2.15, 1H, dd, J = 12.0, 8.6 Hz）说明 H-4 与 H-3、H-5 处于反式，H-1 与 H-9、H-5 与 H-6α 没有耦合说明 H-1 与 H-9、H-5 与 H-6α 的二面角为 90°左右，依据以上结果确定化合物 **1** 的结构为 1β-羟基-3α-甲氧基-7-羰基-8β-甲氧基环烯醚萜酸对羟基苯乙醇酯，命名为丁香苦素 C。其 NMR 数据见表 1。

化合物 **2**：白色针状固体（EtOAc），mp 151.0～152.5 ℃，^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 9.21 (1H, s, Ar-OH), 7.02 (2H, d, J = 8.0 Hz, H-2′, 6′), 6.67 (2H, d, J = 8.0 Hz, H-3′, 5′), 5.01 (1H, d, J = 8.8 Hz, H-3), 4.79 (1H, br s, H-1), 4.19 (2H, m, H-α), 3.37 (3H, s, 1-OCH_3), 2.75 (2H, t, J = 6.8 Hz, H-β), 2.67

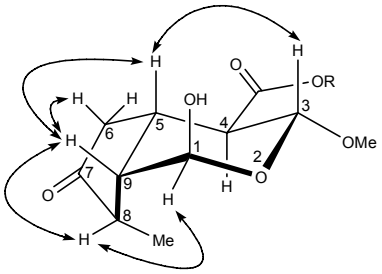

图 2　化合物 1 主要的 NOESY 相关

Fig. 2　Key NOESY correlations of compound 1

表 1　化合物 1 在 DMSO-d_6 中的 NMR 数据

Table 1　NMR data of compound 1 in DMSO-d_6

碳位	^{13}C-NMR	^{1}H-NMR
1	92.0	5.18 (1H, d, *J* = 4.4 Hz)
3	98.0	4.96 (1H, d, *J* = 8.6 Hz)
4	48.7	2.12 (1H, dd, *J* = 12.0, 8.6 Hz)
5	32.2	2.64 (1H, m)
6	41.9	2.29 (1H, dd, *J* = 18.3, 7.7 Hz)
7	217.3	
8	46.1	2.15 (1H, dd, *J* = 12.0, 6.8 Hz)
9	42.4	1.84 (1H, dd, *J* = 12.0, 8.6 Hz)
10	12.8	0.96 (3H, d, *J* = 6.8 Hz)
11	171.8	
1′	127.7	
2′	129.7	7.01 (2H, d, *J* = 8.8 Hz)
3′	115.1	6.66 (2H, d, *J* = 8.8 Hz)
4′	155.9	
α	65.2	4.19 (2H, m)
β	33.5	2.75 (2H, t, *J* = 6.8 Hz)
Ph-OH		9.19 (1H, s)
1-OH		6.71 (1H, d, *J* = 4.4 Hz)
-OCH_3	54.5	3.27 (3H, s)

(1H, m, H-5), 2.30 (1H, dd, *J* = 18.4, 7.6 Hz, H-6), 2.10 (2H, m, H-8), 1.90 (2H, m, H-6), 0.99 (3H, d, *J* = 6.9 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 217.1 (C-7), 172.0 (C-11), 155.9 (C-4′), 129.8 (C-2′, 6′), 127.7 (C-1′), 115.1 (C-3′, 5′), 99.0 (C-1), 88.3 (C-3), 65.1 (C-α), 54.3 (C-OCH_3), 50.4 (C-4), 44.6 (C-8), 42.2 (C-9), 42.1 (C-6), 33.5 (C-β), 32.6 (C-5), 12.7 (C-10)。与文献数据完全一致[5]，鉴定化合物 **2** 为丁香苦素 A。

化合物 **3**：白色无定形固体（EtOAc），^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 9.18 (1H, s, Ar-OH), 7.36 (1H, s, H-3), 7.34 (1H, d, *J* = 4.8 Hz, H-1), 7.03 (2H, d, *J* = 8.4 Hz, H-2′, 6′), 6.66 (2H, d, *J* = 8.4 Hz, H-3′, 5′), 5.41 (1H, d, *J* = 4.8 Hz, H-1), 4.16 (2H, m, H-α), 2.92 (1H, ddd, *J* = 11.3, 10.0, 7.1 Hz, H-5), 2.77 (2H, t, *J* = 6.8 Hz, H-β), 2.54 (1H, dq, *J* = 6.8, 6.4 Hz, H-8), 2.47 (1H, dd, *J* = 7.1, 6.8 Hz, H-9), 2.32 (1H, dd, *J* = 18.3, 10.0 Hz, H-6), 1.94 (1H, d, *J* = 18.3 Hz, H-6), 1.00 (3H, d, *J* = 6.8 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 217.3 (C-7), 166.6 (C-11), 155.8 (C-4′), 151.3 (C-3), 129.8 (C-2′, 6′), 128.2 (C-1′), 115.2 (C-3′, 5′), 109.6 (C-4), 91.9 (C-1), 64.5 (C-α), 45.6 (C-8), 41.8 (C-6), 39.1 (C-9), 33.7 (C-β), 27.2 (C-5), 8.8 (C-10)。与文献数据完全一致[5]，鉴定化合物 **3** 为丁香苦素 B。

化合物 **4**：浅黄色无定形固体，^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 9.16 (1H, br s, Ar-OH), 7.51 (1H, s, H-3), 7.02 (2H, d, *J* = 8.4 Hz, H-2‴, 6‴), 6.66 (2H, d, *J* = 8.4 Hz, H-3‴, 5‴), 5.95 (1H, q, *J* = 6.8 Hz, H-8), 5.86 (1H, br s, H-1), 4.66 (1H, d, *J* = 7.6 Hz, H-1′), 4.27 (1H, d, *J* = 11.6 Hz, H-6″), 4.20 (1H, d, *J* = 7.6 Hz, H-1″), 4.02 (1H, m, H-6″), 3.88 (1H, m, H-5), 3.82 (1H, m, H-1α), 3.67 (1H, d, *J* = 11.6 Hz, H-2α), 3.61 (3H, s, -OCH_3), 3.58 (1H, m, H-6′a), 3.45 (1H, dd, *J* = 11.6, 6.0 Hz, H-6′b), 3.34 (1H, t, *J* = 7.6 Hz), 3.30～2.90 (5H, m, H-Glc), 2.73 (2H, t, *J* = 7.2 Hz, H-β), 2.66 (1H, dd, *J* = 14.8, 4.0 Hz, H-6a), 2.41 (1H, dd, *J* = 14.8, 8.8 Hz, H-6b), 1.66 (3H, d, *J* = 6.8 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 173.1 (C-7), 168.7 (C-11), 156.8 (C-4‴), 155.2 (C-3), 130.9 (C-2‴,6‴), 130.7 (C-1‴), 130.5 (C-9), 125.0 (C-8), 116.1 (C-3‴,5‴), 109.4 (C-4), 104.4 (C-1″), 100.3 (Glc-1′), 95.2 (C-1), 78.4 (Glc-5′), 77.9 (C-5‴), 75.1 (C-3″), 75.0 (C-3′), 72.2 (C-2′), 72.1 (C-2″), 71.8 (C-4′), 71.6 (C-4″), 71.5 (C-α), 65.0 (C-6″), 62.7 (C-6′), 52.0 (C-OCH_3), 41.3 (C-6), 35.3 (C-β), 31.8 (C-5), 13.7 (C-10)。与文献数据一致[6,7]，故鉴定化合物 **4** 为(8*E*)-女贞子苷。

化合物 **5**：白色固体粉末（MeOH），mp 96.1～99.5 ℃。^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.45 (1H, s, H-3), 7.02 (2H, d, *J* = 8.4 Hz, H-2″, 6″), 6.65 (2H, d, *J* = 8.4 Hz, H-3″, 5″), 5.96 (1H, q, *J* = 7.0 Hz, H-8), 5.91 (1H, br s, H-1), 4.80 (1H, d, *J* = 7.6 Hz, H-1′), 4.16 (2H, m, H-α), 3.87 (1H, dd, *J* = 11.8, 6.7 Hz,

H-5), 3.86 (3H, s, H-OCH_3), 3.21～3.19 (5H, m, H-Glc), 3.08 (1H, m, H-Glc), 2.73 (2H, t, J = 6.6 Hz, H-β), 2.66 (1H, dd, J = 14.5, 6.7 Hz, H-6a), 2.42 (1H, dd, J = 14.5, 11.8 Hz, H-6b), 1.66 (3H, d, J = 7.0 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 170.7 (C-7), 166.2 (C-11), 155.3 (C-3), 153.4 (C-4″), 129.7 (C-2″, 6″), 129.1 (C-9), 128.7 (C-1″), 123.1 (C-8), 114.9 (C-3″, 5″), 107.7 (C-4), 98.8 (C-1′), 92.9 (C-1), 73.1 (C-5′), 70.0 (C-3′), 69.9 (C-2′), 69.7 (C-4′), 60.9 (C-6′), 51.2 (C-OCH_3), 39.9 (C-6), 34.8 (C-β), 30.0 (C-5), 13.0 (C-10)。与文献数据完全一致[7]，故鉴定化合物 **5** 为(8*E*)-女贞苷。

化合物 **6**：白色粉末（EtOAc），mp 106.5～109.6 ℃。^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.36 (1H, s, H-3), 7.03 (2H d, J = 8.4 Hz, H-2″, 6″), 6.68 (2H, d, J = 8.4 Hz, H-3″, 5″), 5.41 (1H, s, H-1), 4.49 (1H, d, J = 8.0 Hz, H-6′), 4.16 (2H, m, H-α), 3.75～2.90 (6H, m, H-Glc), 2.92 (1H, m, H-5), 2.78 (2H, t, J = 6.8 Hz, H-β), 2.54 (1H, m, H-8), 2.47 (1H, m, H-9), 2.30 (1H, m, H-6), 1.94 (1H, m, H-6), 1.01 (3H, d, J = 6.8 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 218.1 (C-7), 167.5 (C-11), 157.4 (C-4″), 152.7 (C-3), 131.4 (C-2″, 6″), 130.3 (C-1″), 116.7 (C-3″, 5″), 111.4 (C-4), 100.5 (C-1′), 95.2 (C-1), 78.6 (C-5′), 78.4 (C-3′), 75.0 (C-2′), 72.1 (C-4′), 66.1 (C-α), 63.4 (C-6′), 45.6 (C-9), 44.4 (C-8), 43.4 (C-6), 35.5 (C-β), 28.2 (C-5), 14.2 (C-10)。与文献数据基本一致[8]，故鉴定化合物 **6** 为丁香苦苷。

化合物 **7**：淡黄色粉末（EtOAc），mp 116.5～118.5 ℃。^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.40 (1H, s, H-3), 6.71 (1H, d, J = 8.0 Hz, H-5″), 6.68 (1H, d, J = 1.6 Hz, H-2″), 6.47 (1H, dd, J = 8.0, 1.6 Hz, H-6″), 5.55 (1H, d, J = 2.8 Hz, H-1), 4.50 (1H, d, J = 8.0 Hz, H-1′), 4.16 (2H, m, H-α), 3.80～3.00 (6H, m, H-Glc), 2.92 (1H, m, H-5), 2.71 (2H, t, J = 7.2 Hz, H-β), 2.58 (1H, m, H-8), 2.47 (1H, m, H-9), 2.30 (1H, m, H-6a), 1.94 (1H, m, H-6b), 1.05 (3H, d, J = 6.8 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 217.3 (C-7), 166.6 (C-11), 151.3 (C-3), 135.8 (C-3″), 134.3 (C-4″), 129.8 (C-2″), 128.2 (C-1″), 115.2 (C-5″), 113.4 (C-6″), 109.6 (C-4), 98.8 (C-1′), 91.9 (C-1), 78.6 (C-5′), 78.4 (C-3′), 75.0 (C-2′), 72.1 (C-4′), 64.5 (C-α), 63.4 (C-6′), 45.6 (C-8), 41.8 (C-6), 39.1 (C-9), 33.7 (C-β), 27.2 (C-5), 8.8 (C-10)。与文献数据基本一致[9]，故鉴定化合物 **7** 为 syringopicroside B。

化合物 **8**：白色固体 (MeOH)，mp 123.5～125.0 ℃；^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.57 (1H, s, H-3′), 7.50 (1H, s, H-3), 7.28 (2H d, J = 8.4 Hz, H-2″, 6″), 6.97 (2H, d, J = 8.4 Hz, H-3″, 5″), 6.02 (1H, q, J = 7.0 Hz, H-8′), 5.96 (1H, s, H-1′), 5.95 (1H, q, J = 7.0 Hz, H-8), 5.86 (1H, s, H-1), 4.67 (1H, d, J = 7.6 Hz, H-Glc-1′), 4.64 (1H, d, J = 7.6 Hz, H-Glc-1), 4.27 (1H, dd, J = 10.4, 2.0 Hz, H-Glc-6″), 4.23 (1H, d, J = 7.6 Hz, H-Glc-1″), 4.05 (1H, dd, J = 10.4, 2.0 Hz, H-Glc-6′a), 4.02 (1H, dd, J = 10.4, 2.0 Hz, H-Glc-6), 3.97 (1H, dd, J = 10.4, 5.6 Hz, H-Glc-6″), 3.86 (2H, m, H-α), 3.72 (1H, dd, J = 10.4, 5.6 Hz, H-Glc-6′b), 3.70 (1H, s, H-5′), 3.68 (1H, dd, J = 10.4, 5.6 Hz, H-Glc-6), 3.67 (1H, s, H-5), 3.66 (3H, s, H-OCH_3), 3.60 (3H, s, H-OCH_3), 3.56～3.30 (12H, m, H-Glc), 2.86 (2H, t, J = 6.6 Hz, H-β), 2.72 (1H, dd, J = 14.5, 6.7 Hz, H-6′a), 2.64 (1H, dd, J = 14.5, 6.7 Hz, H-6), 2.53 (1H, dd, J = 14.5, 6.7 Hz, H-6′b), 2.40 (1H, dd, J = 14.5, 6.7 Hz, H-6), 1.70 (3H, d, J = 6.8 Hz, H-10′), 1.66 (3H, d, J = 6.8 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 171.2 (C-7′), 170.1 (C-1), 166.9 (C-11′), 166.8 (C-11), 155.3 (C-3′), 155.2 (C-3), 150.5 (C-4‴), 138.0 (C-1‴), 130.4 (C-2‴, 6‴), 129.9 (C-9′), 129.8 (C-9), 123.8 (C-8′), 123.6 (C-8), 121.9 (C-3‴, 5‴), 108.3 (C-4′), 108.2 (C-4), 103.5 (Glc-1″), 99.9 (C-1′), 99.8 (Glc-1′), 99.6 (C-1), 99.5 (Glc-1), 78.4 (Glc-5′), 78.0 (Glc-5″), 77.9 (Glc-5), 75.2 (Glc-3′), 75.0 (Glc-3″), 74.8 (Glc-3), 72.2 (Glc-2′), 71.7 (Glc-2″), 71.6 (Glc-2), 71.5 (Glc-4′), 71.4 Glc-4″), 71.2 (Glc-4), 65.0 (C-α), 62.7 (Glc-6′), 62.6 (Glc-6″), 62.4 (Glc-6), 52.0 (C-OCH_3), 51.8 (C-OCH_3), 41.3 (C-6′), 41.1 (C-6), 36.6, 35.6 (C-β), 30.7 (C-5′), 30.5 (C-5), 13.8 (C-10′), 13.7 (C-10)。与文献数据基本一致[10]，故鉴定化合物 **8** 为 4-*O*-11-methyl-oleoside-*p*-hydroxyphenyl-(6′-11-methyloleoside)-β-*D*-glucopyranoside。

化合物 **9**：白色固体 (MeOH)，mp 98.3～99.5 ℃；^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.52 (1H, s, H-3), 5.98 (1H, q, J = 6.8 Hz, H-8), 5.87 (1H, s, H-1), 5.31 (1H, d, J = 8.4 Hz, H-1′), 4.64 (1H, d, J = 8.0 Hz, H-1″), 3.88 (1H, dd, J = 9.6, 2.4 Hz, H-5), 3.64 (3H, s,

H-OCH_3), 3.75～2.90 (12H, m, H-Glc), 2.66 (1H, dd, *J* = 11.5, 6.7 Hz, H-6a), 2.42 (1H, dd, *J* = 11.5, 6.7 Hz, H-6b), 1.71 (3H, d, *J* = 6.8 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) *δ*: 170.5 (C-7), 166.2 (C-11), 153.4 (C-3), 129.1 (C-9), 123.1 (C-8), 107.7 (C-4), 99.3 (C-1″), 95.0 (C-1′), 93.3 (C-1), 78.3 (C-5″), 77.8 (C-5′), 76.8 (C-3″), 76.7 (C-3′), 73.7 (C-2″), 72.8 (C-2′), 70.3 (C-4″), 69.8 (C-4′), 61.5 (C-6″), 60.9 (C-6′), 51.9 (C-OCH_3), 39.9 (C-6), 30.1 (C-5), 13.9 (C-10)。与文献数据基本一致[11]，故鉴定化合物 **9** 为 7β-*D*-glucopyranosyl-11-methyloleoside。

化合物 **10**：白色棱状晶体（MeOH），mp 173.1～175.0 ℃。^{1}H-NMR (DMSO-d_6, 400 MHz) *δ*: 7.51 (1H, s, H-3), 7.04 (2H, d, *J* = 8.4 Hz, H-2″, 6″), 6.67 (2H, d, *J* = 8.4 Hz, H-3″, 5″), 5.91 (1H, s, H-1), 4.80 (1H, d, *J* = 7.6 Hz, H-1′), 4.33 (1H, dq, *J* = 13.9, 6.8 Hz, H-8), 4.16 (2H, m, H-α), 3.30～3.00 (6H, m, H-Glc), 2.98 (1H, m, H-5), 2.92 (1H, m, H-9), 2.77 (2H, t, *J* = 6.8 Hz, H-β), 2.32 (1H, dd, *J* = 12.8, 10.0 Hz, H-6a), 1.94 (1H, dd, *J* = 12.8, 110.0 Hz, H-6b), 1.66 (3H, d, *J* = 6.8 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) *δ*: 172.2 (C-7), 166.6 (C-11), 155.8 (C-4″), 151.3 (C-3), 129.8 (C-2″,6″), 128.2 (C-1″), 115.2 (C-3″,5″), 109.6 (C-4), 98.8 (C-1′), 91.9 (C-1), 77.9 (C-5′), 73.1 (C-3′), 70.0 (C-2′), 69.7 (C-4′), 64.5 (C-α), 60.9 (C-6′), 41.8 (C-6), 39.1 (C-9), 33.7 (C-β), 27.2 (C-5), 8.8 (C-10)。与文献数据基本一致[12]，故鉴定化合物 **10** 为 lilacoside。

化合物 **11**：淡黄色晶体，mp 82.9～84.1 ℃；IR、^{1}H-NMR 数据与文献数据一致[3]，鉴定化合物 **11** 为对羟基苯乙醇。

化合物 **12**：白色固体 (MeOH)，mp 132.9～135.0 ℃；^{1}H-NMR (DMSO-d_6, 400 MHz) *δ*: 8.27 (1H, br s, Ar-OH), 7.53 (1H, s, H-3′), 7.51 (1H, s, H-3), 6.97 (2H d, *J* = 8.4 Hz, H-2″, 6″), 6.62 (2H, d, *J* = 8.4 Hz, H-3″, 5″), 5.98 (1H, q, *J* = 7.0 Hz, H-8′), 5.97 (1H, q, *J* = 7.0 Hz, H-8), 5.87 (1H, s, H-1′), 5.86 (1H, s, H-1), 4.67 (1H, d, *J* = 7.6 Hz, H-Glc-1′), 4.64 (1H, d, *J* = 7.6 Hz, H-Glc-1), 4.53 (1H, t, *J* = 7.6 Hz, H-Glc-2″), 4.27 (1H, dd, *J* = 10.4, 2.0 Hz, H-6″), 4.23 (1H, d, *J* = 7.6 Hz, H-Glc-1″), 4.05 (1H, dd, *J* = 10.4, 2.0 Hz, H-Glc-6′), 4.02 (1H, dd, *J* = 10.4, 2.0 Hz, H-Glc-6), 3.97 (1H, dd, *J* = 10.4, 5.6 Hz, H-Glc-6″), 3.86 (2H, m, H-α), 3.72 (1H, dd, *J* = 10.4, 5.6 Hz, H-Glc-6′), 3.70 (1H, s, H-5′), 3.68 (1H, dd, *J* = 10.4, 5.6 Hz, H-Glc-6), 3.66 (1H, s, H-5), 3.64 (3H, s, H-OCH_3), 3.62 (3H, s, H-OCH_3), 3.56～3.30 (12H, m, H-Glc), 2.86 (2H, t, *J* = 6.6 Hz, H-β), 2.72 (1H, dd, *J* = 14.5, 6.7 Hz, H-6′a), 2.65 (1H, m, H-6a), 2.53 (1H, dd, *J* = 14.5, 6.7 Hz, H-6′b), 2.44 (1H, dd, *J* = 14.5, 6.7 Hz, H-6b), 1.71 (3H, d, *J* = 6.8 Hz, H-10′), 1.67 (3H, d, *J* = 6.8 Hz, H-10)；^{13}C-NMR (DMSO-d_6, 100 MHz) *δ*: 171.2 (C-7′), 170.1 (C-7), 166.9 (C-11′), 166.8 (C-11), 154.2 (C-3′), 154.0 (C-3), 150.5 (C-4‴), 138.0 (C-1‴), 130.4 (C-2‴, 6‴), 129.9 (C-9′), 129.8 (C-9), 123.8 (C-8′), 123.6 (C-8), 121.9 (C-3‴, 5‴), 108.3 (C-4′), 108.2 (C-4), 103.5 (C-Glc-1″), 99.9 (C-1′), 99.8 (C-Glc-1′), 99.5 (C-1), 99.5 (C-Glc-1), 73.5 (C-Glc-5′), 73.4 (C-Glc-5″), 73.2 (C-Glc-5), 71.7 (C-Glc-3′), 71.6 (C-Glc-3″), 71.5 (C-Glc-3), 71.1 (C-Glc-2′), 71.0 (C-Glc-2″), 70.6 (C-Glc-2, 4′), 70.5 (C-Glc-4, 4″), 61.8 (C-Glc-6′), 61.7 (C-Glc-6″), 60.3 (C-Glc-6), 52.0 (C-OCH_3), 51.8 (C-OCH_3), 41.3 (C-6′), 41.1 (C-6), 35.6 (C-β), 30.8 (C-5′), 30.6 (C-5), 13.9 (C-10′), 13.6 (C-10)。以上数据与文献基本一致[13]，故鉴定化合物 **12** 为 2-(*p*-hydroxyphenyl)-ethyl-2, 6-bis (2*S*, 3*E*, 4*S*)-3-ethylidene-2-(β-*D*-gluco-pyranosyloxy)-3, 4-dihydro-5-(methoxycarbonyl)-2H-pyran-4-acetate。

化合物 **13**：无色无定形体，^{1}H-NMR (DMSO-d_6, 400 MHz) *δ*: 6.95 (2H, d, *J* = 8.4 Hz, H-2, 6), 6.66 (2H, d, *J* = 8.4 Hz, H-3, 5), 4.74 (2H, t, *J* = 7.2 Hz, H-α), 3.09 (2H, t, *J* = 7.2 Hz, H-β), 2.75 (2H, q, *J* = 3.6 Hz, H-2′), 1.19 (3H, t, *J* = 7.2 Hz, H-3′)；^{13}C-NMR (DMSO-d_6, 100 MHz) *δ*: 157.1 (C-1′), 143.2 (C-4), 130.3 (C-2, 6), 126.4 (C-1), 115.9 (C-3, 5), 61.9 (C-α), 36.5 (C-β), 25.4 (C-2′), 14.9 (C-3′)。综合以上数据鉴定化合物 **13** 为对羟基苯乙醇丙酸酯。

化合物 **14**：白色粉末，^{1}H-NMR (DMSO-d_6, 400 MHz) *δ*: 7.28 (1H, s, H-2″), 7.23 (1H, d, *J* = 8.1 Hz, H-6″), 6.85 (1H, d, *J* = 8.1 Hz, H-5″), 5.47 (1H, br s, H-15), 4.70 (1H, dd, *J* = 11.5, 4.7 Hz, H-3), 3.52 (1H, dd, *J* = 9.3, 6.2 Hz, H-21), 3.08 (2H, t, *J* = 7.5 Hz, H-3′), 2.80 (2H, t, *J* = 7.5 Hz, H-2′), 2.31 (1H, d, *J* = 14.3 Hz, H-27), 2.15 (2H, m, H-9, 16), 2.01 (2H, m, H-16, 19), 1.90 (2H, m, H-2, 12), 1.85 (1H, d, *J* = 14.3 Hz, H-27), 1.83 (1H, m, H-13), 1.75 (1H, m, H-20),

1.74 (1H, m, H-11), 1.68 (1H, m, H-1), 1.64 (2H, m, H-2, 20), 1.39 (2H, m, H-6, 7), 1.38 (3H, m, H-6, 12, 17), 1.19 (3H, s, H-30), 1.16 (1H, m, H-7), 1.12 (1H, m, H-11), 1.10 (3H, s, H-29), 0.94 (1H, m, H-1), 0.90 (3H, s, H-26), 0.89 (3H, s, H-24), 0.86 (3H, s, H-23), 0.80 (1H, m, H-5), 0.78 (6H, s, H-25, 28), 0.74 (1H, m, H-9)。以上数据与文献一致[11]，故鉴定化合物 **14** 为 21α-hydroxy-serrat-14-en-3β-yl-dihydrocaffeate。

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