

臭灵丹中五个新的桉烷类衍生物*

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FIVE NEW EUDESMANE DERIVATIVES FROM
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关键词 臭灵丹, 桉烷型倍半萜, 倍半萜甙, 臭灵丹甙 A, 臭灵丹甙 B 桉烷类衍生物, 化学成分
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A, Pterodontoside B

Three eudesmanoic acids (1~3) and two eudesmanoic acid glucosides (4~5) were isolated from the n-BuOH extract of the title plant.

Compound 1 was isolated as colorless crystals. EI and FABMS showed its molecular ion peak at m/z 266, corresponding to the molecular formula $C_{15}H_{22}O_4$. The 1H and ^{13}C NMR spectra of compound 1 showed some similarities with those of compound 6, previously isolated from this species (Li *et al.*, 1996). Comparing the ^{13}C NMR spectra between 1 and 6 showed that, in the ^{13}C NMR spectrum of 1, the C-10 and C-8 signals were shifted downfield, while C-7 was upfield shifted, which suggested the presence of another OH group at C-9. By the coupling pattern of H-9 of 1 (Table 1), the 9-OH group was assigned to be β -orientation, which was in agreement with the demonstration model.

Compound 2 has the same molecular weight as that of 1 (m/z 266). Combined with the results of elemental analysis, the molecular formula of 2 could be proposed as $C_{15}H_{22}O_4$. The lowfield shift of C-2 and C-4 of 2 (Table 2), when comparing its ^{13}C NMR data with those of 1 and 6, diagnostically indicated the presence of a 3-OH (Table 2). Since H-3 only showed a small coupling with H-4 (5.0Hz) and other two small ones with H-2 (5.0, 5.0Hz), the 3-OH could be deduced to be an α -configuration.

The 1H and ^{13}C NMR spectra of 3 were partially similar to those of ilicic acid (Herz, 1966). However, a lowfield broadened triplet appeared at δ 4.56($J=3.3Hz$) in the 1H NMR spectrum of 3, corresponding to the ^{13}C resonance at δ 67.82(CH) (Table 2). The chemical shifts of C-1 and C-3 of 3 were remarkable in a lowfield (Table 2), thus the presence of a 2-OH was clear. The small couplings of H-2 (with H-1 and H-3) disclosed that the OH group should be a β -orientation.

FABMS of 4 gave the $[M+H]^+$ peak at m/z 413, and a base peak due to the lossing of a glucose

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molecule at m/z 233. The ^1H and ^{13}C NMR spectra of **4** also showed the presence of a β -D-glucose (Tables 1, 2). Acid hydrolysis of **4** gave the glucose and an aglycone **4a**, which has an identical R_f value, and the same ^1H and ^{13}C NMR data, with those of a known compound **6** (Li *et al.*, 1996). Inspection of the ^{13}C NMR spectra of **4** and **6** indicated that C-1 of **4** was apparently lowfield shifted, while C-2 and C-10 were both highfield shifted (Table 2) when comparing with those of **6**, thus requiring the β -D-glucose to be connected to the C-1 of the aglycone **6**.

Table 1 ^1H NMR data of compounds 1~5 (400 MHz, $\text{C}_3\text{D}_3\text{N}$)

| H | 1 | 2 | 3 | 4 | 5 |
|------|--------------------------------|-----------------------------|-------------------------------|------------------------------|------------------------|
| 1 | 3.89 dd (11.6, 4.3) | 3.73 dd (11.5, 4.3) | 2.19 dd (13.7, 3.6) | 3.64 dd (11.6, 4.0) | 1.26 m |
| 1' | — | — | 2.59 brd(13.5) | — | 1.50 m |
| 2 | 2.48 m | 2.49 m | 4.56 brt(3.3) | 2.25 ddt (10.8, 4.0, 3.5) | 1.74 mm |
| 2' | 2.08 ddd (11.6, 11.6, 4.0) | 2.43 m | — | 2.04 m | 1.42 m |
| 3 | 1.69 m | 4.22 ddd (5.0, 5.1, 5.0) | 1.49 dd (13.9, 3.6) | 1.52 m | 1.56 mm |
| 3' | 1.69 m | — | 1.96 brd(14.0) | 1.52 m | 1.56 m |
| 4 | 2.48 m | 2.93 brdq(7.0, 5.0) | — | 2.38 m | 2.94 m |
| 5 | — | — | 1.85 m | — | — |
| 6 | 5.48 brs | 5.68 brs | 2.75 brd(12.4) | 5.47 brs | 5.45 brs |
| 6' | — | — | 1.72 m | — | — |
| 7 | 3.86 m | 3.72 m | 2.98 tt(12.5, 3.4) | 3.60 m | 3.58 m |
| 8 | 2.50 m | 2.55 m | 1.72 m | 2.06 m | 2.50 m |
| 8' | 2.00 ddd (11.6, 11.6, 11.6) | 1.69 m | 1.84 m | 1.56 m | 1.56 m |
| 9 | 4.21 dd (12.0, 3.2) | 1.56 m | 1.32 ddd (12.6, 12.6, 4.3) | 1.50 m | 3.88 dd (12.2, 3.0) |
| 9' | — | 2.33 m | 1.54 m | 1.94 m | — |
| 12 | — | — | — | — | — |
| 13 | 5.69 brs | 5.73 brs | 5.72 s | 5.63 brs | 5.58 brs |
| 13' | 6.52 brs | 6.56 brs(1.2) | 6.52 d(1.1) | 6.50 d(1.4) | 6.44 d(1.6) |
| 14 | 1.52 s | 1.47 s | 1.54 s | 1.24 s | 1.36 s |
| 15 | 1.22 d(7.6) | 1.50 d(6.9) | 1.79 s | 1.10 d(7.6) | 1.15 d(7.6) |
| 1'' | — | — | — | 4.89 d(7.7) | 4.97 d(7.7) |
| 2'' | — | — | — | 4.00 t(8.4) | 4.05 t(8.6) |
| 3'' | — | — | — | 3.95 m | 3.98 m |
| 4'' | — | — | — | 4.27 m | 4.27 m |
| 5'' | — | — | — | 4.24 m | 4.25 m |
| 6''1 | — | — | — | 4.54 dd(11.7, 2.4) | 4.50 dd(11.8, 2.7) |
| 6''2 | — | — | — | 4.39 dd(11.7, 5.2) | 4.36 dd(11.7, 5.0) |

FABMS and EIMS spectra disclosed that compound **5** owned the same molecular ion peak with that of **4** at m/z 412. Its ^1H and ^{13}C NMR spectra disclosed the presence of a β -D-glucose in the molecule (Tables 1, 2). Scrutiny of the ^{13}C NMR data of **5**, coupled with comparisons with those of **4** and a known compound pterodontronic acid **7** (Li *et al.*, 1996), demonstrated that the lowfield C-1 was absent while a

lowfield C-9 appeared in compound **5** at δ 87.79(CH). Meanwhile, the C-8 signal was lowfield shifted (ca 5.45 ppm, Table 2), as well as the C-10 resonance of **5** changed to δ 40.23(C) from δ 35.22(C) in the case of **7**. The remaining skeletal carbon signals of **5** were nearly identical with those of **7** (Li *et al.*, 1996), indicating that the sugar was connected at C-9. Furthermore, H-9 showed a large coupling (12.0 Hz) and a small one (3.0Hz) with H-8, thus eliminating the possibility of a H-9 β which would be a triplet with small coupling.

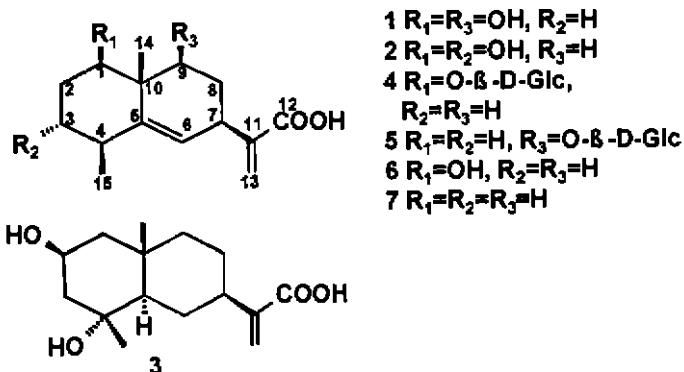


Table 2 ^{13}C NMR data of compounds 1~7 (100.6 MHz, C_5D_5N)

| C | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-----|--------|--------|--------|--------|--------|--------|--------|
| 1 | 79.36 | 77.20 | 50.23 | 85.92 | 38.42 | 79.37 | 42.76 |
| 2 | 26.45 | 36.69 | 67.82 | 23.02 | 17.52 | 27.00 | 18.46 |
| 3 | 30.34 | 69.86 | 47.82 | 30.26 | 33.85 | 30.76 | 34.08 |
| 4 | 38.41 | 46.60 | 70.86 | 39.01 | 37.91 | 38.40 | 39.04 |
| 5 | 147.38 | 147.43 | 55.56 | 147.80 | 147.47 | 148.09 | 148.67 |
| 6 | 125.53 | 127.97 | 27.36 | 126.18 | 123.53 | 125.99 | 124.91 |
| 7 | 37.70 | 39.44 | 41.39 | 39.01 | 38.43 | 39.14 | 39.62 |
| 8 | 30.34 | 27.15 | 27.63 | 26.77 | 33.03 | 27.33 | 27.58 |
| 9 | 81.36 | 38.76 | 45.92 | 38.23 | 87.79 | 38.65 | 42.59 |
| 10 | 44.27 | 40.50 | 34.75 | 40.06 | 40.23 | 40.94 | 35.22 |
| 11 | 146.77 | 147.08 | 148.39 | 147.51 | 146.75 | 147.84 | 148.02 |
| 12 | 169.58 | 169.76 | 170.04 | 169.66 | 169.53 | 170.05 | 169.87 |
| 13 | 123.11 | 122.94 | 121.52 | 122.72 | 122.62 | 122.34 | 125.86 |
| 14 | 14.99 | 21.59 | 20.84 | 22.05 | 21.17 | 21.21 | 28.02 |
| 15 | 24.02 | 16.88 | 25.63 | 23.37 | 23.79 | 23.40 | 23.91 |
| 1'' | — | — | — | 102.37 | 106.54 | — | — |
| 2'' | — | — | — | 75.29 | 75.88 | — | — |
| 3'' | — | — | — | 78.32 | 78.11 | — | — |
| 4'' | — | — | — | 72.06 | 71.94 | — | — |
| 5'' | — | — | — | 78.78 | 78.72 | — | — |
| 6'' | — | — | — | 63.18 | 63.72 | — | — |

1 β ,9 β -Dihydroxy-5,11(13)-dien-eudesman-13-oic acid (1): $C_{15}H_{22}O_4$, colourless prisms, mp 210~211 $^{\circ}C$ (MeOH). FAB-MS (positive) (m/z): 267 [$M+H$] $^{+}$ (12), 249(42), 231(100), 159(48).

1 β ,3 α -Dihydroxy-5,11(13)-dien-eudesman-13-oic acid (2): $C_{15}H_{22}O_4$, colourless gum (MeOH). EI-MS (m/z): 266 [M] $^{+}$ (8), 248(45), 230(74), 202(100).

2 β -Hydroxy-ilicic acid (3): $C_{15}H_{24}O_4$, needles, mp 198~199 $^{\circ}C$ (MeOH). FAB-MS (positive) (m/z): 269[M+H] $^{+}$ (5), 251(23), 233(100), 223(14), 161(21).

Pterodontoside A (1 β -Hydroxy-pterodonic acid-1-O- β -D-glucopyranoside) (4): $C_{21}H_{32}O_8$, needles, mp 248~249 $^{\circ}C$ (dec.) (MeOH). FAB-MS (positive) (m/z): 413[M+H] $^{+}$ (7), 251(14), 233(100), 215(12).

Pterodontoside B (9 β -Hydroxy-pterodonic acid-9-O- β -D-glucopyranoside) (5): $C_{21}H_{32}O_8$, powders, mp 255~256 $^{\circ}C$ (dec.) (MeOH). FAB-MS (positive) (m/z): 413[M+H] $^{+}$ (9), 251(25), 233(68), 205(100), 149(33), 123(43).

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1. 研究论文及简报的基本格式参照本刊 1993 年(15 卷)第 1—2 期。
2. 植物材料应附正确的拉丁学名、产地、数量和制备方法。
3. 化学结构图须另页绘制,基团标注无误,在文稿内注明插图位置。常见化合物的结构不必给出。表插入文中适当位置,图表应附相应的英文。
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6. 新化合物采用 IUPAC 命名规则给出一个完整的系统名,若有必要可再取一个得体的俗名。文中化合物第一次出现时若注有编号,下文均以编号代表。
7. 每个化合物尽可能标出得率,如: 化合物 3 (510mg, 0.0031%)。结晶须指明所用溶剂,如: 白色针晶 (MeOH), 熔点的表示法,如: mp 259—261 $^{\circ}C$ 。液体化合物的折射率表示法,如 n_D^{25} 1.653。
8. 元素分析表示法,如: 已知化合物(Found: C, 62.9; H, 5.4. Calc. for $C_{13}H_{13}ON_4$: C, 62.9; H, 5.3%)。新化合物(Found: C, 62.9; H, 5.4. $C_{13}H_{13}ON_4$ requires: C, 62.9; H, 5.3%)。
9. 比旋度的表示法: $[\alpha]_D^{25}$ 测定值 $^{\circ}$ (所用溶剂; c 指 100 mL 溶剂里化合物的克数), 如 $[\alpha]_D^{25} +32.2^{\circ}$

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