中山大学学报 (自然科学版)
第 37卷 第 2期 ACTA SCIENTIARUM NATURALIUM Vol. 37 No. 2
1998年 3月 UNIVERSITATIS SUNYATSENI Mar. 1998

The Constituents of Diterpenes from *Isodon enanderianus* *

Zhang Kun[1)] Wang Yanhong[1,2)] Chen Yaozu[1,3)]
Sun Handong[4)] Lin Zhongwen[4)]

(1) State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000; 2) School of Chemistry and Chemical Engineering, Zhongshan University; 3) Department of Chemistry, Zhejiang University; 4) Laboratory of Phytochemistry, Kunming Institute of Botany)

Abstract Two diterpenes were isolated from the leaves of *Isodon enanderianus*. Their structures were elucidated on the basis of spectral analysis. The constituents of *I. enanderianus* have not been reported before.

Keywords *Isodon enanderianus*, Labiatae, *ent*-kaurene, diterpene
Classificational number O 624.421

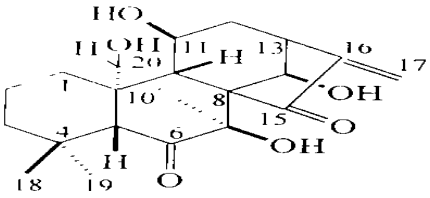
The diterpenes of *Isodon* species have different bioactives, such as cytotoxicity, antitumor activity, inhibition of oxidative phosphorylation and so on[1]. *Isodon enanderianus* (Labiatae) is one kind of plant in this family, and mainly distributed in Kaiyuan, Yuanjiang and Shiping in Yunnan Province[2]. The leaves of this plant are used as a traditional medicine for stomatitis, eczema and beriberi in these regions. As systematic part of an investigation of the bioactive compounds in *Isodon*, two diterpenoids have been isolated from a methanol extract of the leaves of *I. enanderianus*. The structure elucidation of the two compounds is the subject of this paper.

1 Results and discussion

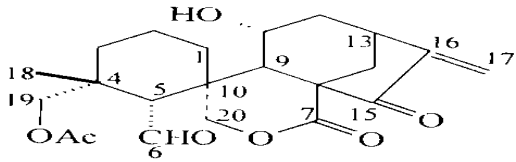
Compound **1** $C_{20}H_{26}O_6$ ($[M+1]^+$ *m/z* 363) showed the presence of two methyl carbons, four methlenes, six methines, four quaternary carbons, two olefinic carbons and two ketonic carbons in its ^{13}C NMR and DEPT spectra. It contains a five-membered ring with a ketone conjugated with an exo-methylene group from the following spectral data: UV λ_{max}, 230 nm ($\lg\varepsilon$ 3.74); IR ν_{max}/cm^{-1}, 1 710 and 1 641; ^1H NMR δ, 6.18 and 5.40 (each 1H, s); ^{13}C NMR δ, 152.5 (s), 117.1 (t) (exo-methylene), 211.7 (s) (ketone). The above data and the presence of two tertiary methyl signals at δ1.29 (s) and 0.86 (s), a methine signal at δ4.58 (1H, br. s) and δ80.8 (d) suggested that this compound has an 20-oxy-*ent*-kaur-16-en-15-one nucleus as the basic skeleton[1].

Compound **1** was found to have two secondary hydroxyl groups based on the following

* 中国科学院昆明植物研究所化学植物开放实验室开放基金资助项目
收稿日期: 1997-07-25 张火昆, 男, 34岁, 副教授



1



2

spectroscopic data IR ν_{max} /cm^{-1}, 3 302 and 3 227; ^{1}H NMR W, 5.24 (1H, m) and 5.90 (1H, br. s); ^{13}C NMR W, 73.2 and 65.1 (each CH). The locations of these hydroxyl groups were deduced as follows. Between **1** and kamebakaurinin[3], the similiarity of chemical shift value of carbons (C-11 and C-14) suggested that there were two oxygen substituents at the 1β and 14β-position respectively[3]. Meanwhile, in comparison of **1** with kamebakaurinin, the following differences were observed. (i) The presence of a quaternary carbon at W204.5 (s) and the increase of chemical shift value of C-5 (ΔW10.0) in **1** suggested that there was an carbonyl carbon at C-6 in place of the methylene carbon in kamebakaurinin. (ii) The presences of a quaternary carbon at W90.1 (s) and a methine at W80.8 (d) in **1**, which correspondingly took the place of a methine and a methylene in kamebakaurinin, suggested that a ring was formed between C-7 and C-20, and that there was a hydroxy group at C-7. Thus, **1** was elucidated as 7β, 1β, 14β, 20-tetrahydroxy-*ent*-kaur-16-en-6, 15-dione[4].

Compound **2**, colorless needles. $C_{22}H_{28}O_7$ ([M]$^+$ *m*/*z* 404). It contains a five membered ring with a conjugated exo-methylene group from the following spectral data: UV λ_{max}, 232 nm (lg X3.96); IR ν_{max} /cm^{-1}, 1 735 and 1 645. ^{1}H NMR W, 6.05 and 5.40 (each 1H, br. s); ^{13}C NMR W, 150.9 (s), 118.1 (t) (exo-methylene) and 203.7 (s) (ketone). Its characteristic IR absorptions at 1 736, 1 239 and 1 059 cm^{-1} and the presence of a quaternary carbon at W171.2 (s) suggested that there was a lactone group in **2**. In addition, the more broad peaks in the ^{1}H NMR spectrum and the lack of some carbon signals in the ^{13}C NMR spectrum suggested that **2** was a secokaurane and had a spircone strnucture at C-10 as the basic skeleton[1]. Its IR, MS, ^{1}H NMR, ^{13}C NMR and DEPT spectra showed the similarity to the known compound, trichorabdal **B**[5].

2 Experimental

(1) General. MPs: uncorr; IR KBr; UV: MeOH; ^{1}H NMR (400.134 MHz); ^{13}C NMR (100.62 MHz, broad band and DEPT). pyridine-d_5, TMS as int. standard; EIMS: 70 eV.

(2) Plant material. The leaves of *Isodon enanderianus* were collected in October 1993 in Shiping County, Yunnan Province.

(3) Extraction and isolation. Dried and powdered leaves (4.6 kg) were extracted with 95% EtOH at reflux conditions for three times. The solvent was combined and evaporated under reduced pressure. The left solvent was partitioned with petroleum-ether and EtOAc, respectively. From the layer of EtOAc, a black brown residue (185 g) was obtained and subjected to CC (silica gel, 1 kg) eluted with petroleum ether-Me_2CO (8∶2~5∶5). The fraction (8∶2 part) was further purified by silica gel CC and recrystallization yielded **2**. The fraction (6∶4 part) was purified by siica gel CC yielding **1**.

(4) Physical and spectral data of **1** and **2**. **1**, colorless needles, $C_{20}H_{26}O_6$, θ_{mp} 262~ 264 ℃; UV (MeOH) λ_{max}: 230 nm (lg X3. 74); IR ν_{max} /cm^{-1}: 3 302, 3 273, 3 227, 1 754, 1 710, 1 640, 1 543, 1 046; MS(FAB): 363 ([M+ 1]$^+$), 345, 327, 309, 179; ^{1}H NMR W 3. 22(9β- H, d, *J*= 9. 4 Hz), 5. 24(11α- H, m), 3. 03(12α- H, m), 5. 90(14α- H, s), 6. 18 and 5. 40(17- Ha and 17- Hb, each s), 4. 58(20- H, br. s), 1. 29 and 0. 86(18- Me and 19- Me); ^{13}C NMR W 23. 6(t, C- 1), 19. 5(t, C- 2), 41. 3(t, C- 3), 33. 6 (s, C- 4), 64. 0(d, C- 5), 204. 5(s, C- 6), 90. 1(s, C- 7), 47. 5(s, C- 8), 62. 5(d, C- 9), 60. 2(s, C- 10), 65. 1(d, C- 11), 43. 4(t, C- 12), 43, 8(d, C- 13), 73. 2(d, C- 14), 211. 7(s, C- 15), 152. 5(s, C- 16), 117. 1(t, C- 17), 33. 6(q, C- 18), 23. 6(q, C- 19), 80. 8(d, C- 20).

2, colorless needles, $C_{22}H_{28}O_7$, θ_{mp}: 160~ 162 ℃; UV (MeOH) λ_{max}: 232 nm (lg X 3. 96); IR ν_{max} /cm^{-1}: 3 287, 3 231, 1 736, 1 735, 1 645, 1 376, 1 239, 1 059; MS(EI): 404 ([M]$^+$), 386, 344, 327, 298, 225; ^{1}H NMR W 2. 50(5β- H, overlap), 10. 2(6- CHO, d, *J*= 3. 6 Hz), 3. 53(1β- H, br. s), 3. 12(13β- H, m), 6. 05 and 5. 40(17- Ha and 17- Hb, each br. s), 5. 10 and 4. 05(19- Ha and 19- Hb, each br. s), 5. 18 and 4. 56(20- Ha and 20- Hb, each br. s), 1. 15(18- Me), 1. 95(OAc); ^{13}C NMR W 18. 2(t, C- 2), 28. 1(s, C- 4), 203. 7(d, C- 6), 171. 2(s, C- 7), 38. 6(s, C- 10), 65. 1(d, C- 11), 42. 1(t, C- 12), 35. 2(d, C- 13), 203. 7(s, C- 15), 150. 9(s, C- 16), 118. 1(t, C- 17), 35. 2(q, C- 18), 71. 2(t, C- 19), 170. 4 and 20. 5(OAc).

References

1 Fujita E, Node M. Diterpenoids of *Rabdosia species*. Progress in Chemistry of Organic Natural Products, 1984, 46 77~ 157

2 Wu C Y, Li H W. Flora reipublicae popularis sinicae 66(2). Beijing: Beijing Academic Press, 1977

3 Takeda Y, Ichihara T, Takaishi Y, et al. Structural elucidation of new diterpenoids isolated from *Rabdosia umbrosa* var. *Ieucantha* F. Kameba. J Chem Soc Perkins Trans(I), 1987 2403~ 2409

4 Fujita T, Sun H D, Takeda Y, et al. Structure of phyllostachysin **A**: novel antineoplastic diterpenoid from *Rabdosia phyllostachys*. J Chem Soc Chem Commun, 1985 1738~ 1739

5 Fujita E, Fuji K, Sai M, et al. The structrue of trichorabdal **B** and transformation into a novel skeleton; X-ray crystal structures. J Chem Soc Chem Commun, 1981 899~ 900

紫毛香茶菜二萜成分研究

张　火焜　王艳红*　陈耀祖　孙汉董　林中文

摘　要　从紫毛香茶菜干叶的乙醇提取物中分离得到 2个二萜化合物, 利用红外、紫外、质谱以及核磁共振波谱等光谱方法, 对这 2个化合物的结构进行了鉴定. 紫毛香茶菜的化学成分尚未见文献报道.

关键词　紫毛香茶菜, 唇形科, 二萜, 对映-贝壳杉烯

分类号　O 624. 421

* 中山大学化学与化学工程学院, 广州 510275