

思茅松松香中的一个新二萜*

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摘要: 从思茅松 (*Pinus kesiya* var. *langbianensis*) 的松香中分离得到一个新奇的松香烷二萜化合物——思茅松素, 经现代波谱分析将其化学结构确定为 13 (14)-烯-8, 12-环氧-18-松香酸 (1), 同时分离得到 5 个已知化合物, 分别为 abiet-8, 11, 13-trien-15-hydroxy-18-oic acid (2); pimarol (3a); iso-pimarol (3b); abiet-trien-18-oic acid (4); 15-hydroxy abietic acid (5)。

关键词: 思茅松; 思茅松素; 松香烷二萜

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A New Abietane Diterpenoid from the Rosin of *Pinus kesiya* var. *langbianensis* (Pinaceae)*

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Abstract: Szemaoenin, a new abietane diterpenoid with five compounds, has been isolated from the rosin of *Pinus kesiya* var. *langbianensis*. Their chemical structures were elucidated as abiet-13 (14)-en-8, 12-epoxy-18-oic acid (1), abiet-8, 11, 13-trien-15-hydroxy-18-oic acid (2); pimarol (3a); iso-pimarol (3b); abiet-8, 11, 13-trien-18-oic acid (4); 15-hydroxy abietic acid (5); respectively by spectroscopic means.

Key words: *Pinus kesiya* var. *langbianensis*; Abietane diterpenoid; Szemaoenin

Pinus kesiya Royle ex Gord. var. *langbianensis* Gaussen, a species of genus *Pinus* L., is mainly distributed in the southern region of Yunnan Province, China. It has the efficacy of stimulating the menstrual flow, invigorating the circulation of blood, diminishing and relieving pain. (Wu *et al*, 1988) However, Its chemical constituents studies have not been reported in detail up to now. In order to clarify the medicinal value of the plant, the rosin of *Pinus kesiya* var. *langbianensis* was studied for the first time and a novel compound called szemaoenin was isolated together with

five known compounds. In the paper we report the chemical structural elucidation of compound 1 by spectral analyses.

Compound 1, colorless crystals, mp: 166 – 168 °C; $[\alpha]_D^{25} = 73.0^\circ$ ($c = 0.4$, CHCl₃). Its molecular, C₂₀H₃₀O₃, was determined by its EI HRMS (found 318.2197, calcd. 318.2195) and combined with ¹³C NMR (DEPT) spectral data. The IR spectrum showed the presence of carboxyl group (ν_{\max} 3422 cm⁻¹, 1689 cm⁻¹), the cyclic olefinic bond ($\Delta^{13,14}$) at ν_{\max} 2927.7, 991.9, 946.8 cm⁻¹. ¹H-

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and ^{13}C -NMR spectra indicated that it was composed of four methyl, six methylenes, five methines including an olefinic carbon and an oxygen-bearing carbon, five quaternary carbons including an olefinic carbon, a carbon bearing an oxygen and a carboxyl group (Table 1). The above spectral suggested that this compound belonged to an abietane diterpenoid (Mei *et al*, 2000; Gong, 1986). Meanwhile, according to the cross peak in HMBC spectrum, the epoxy is obviously located at C-8 and C-12. Moreover inspection of MS and NMR spectra of **1** suggested the presence of the carboxyl group at C-4 and olefinic bond at C-13, C-14.

Table 1 ^{13}C (125 MHz) and ^1H (400 MHz) NMR data of **1**

No.	^{13}C	^1H	No.	^{13}C	^1H
1	38.69(t)	1.10-1.19(m)	10	39.11(s)	
2	18.89(t)	1.10-1.19(m)	11	32.99(t)	1.10-1.19(m)
3	37.78(t)	1.10-1.19(m)	12	72.48(d)	4.41(t, $J=8\text{Hz}$)
4	47.46(s)		13	141.12(s)	
5	46.36(d)	2.43(dd, $J=7.1, 9.9\text{Hz}$)	14	133.36(d)	5.92(s)
6	18.98(t)		15	36.76(d)	2.14(m)
7	33.56(t)	1.10-1.19(m)	16	17.57(q)	0.96(s)
8	71.69(s)		17	17.82(q)	0.96(s)
9	43.10(d)	2.72(dd, $J=2.2, 2.3\text{Hz}$)	18	181.20(s)	7.78(s)
			19	17.48(d)	1.51(s)
			20	14.94(q)	1.51(s)

According to the ^1H - ^1H COSY and HMQC experiments, all of protons and related carbons were assigned as Table 1. The signals at δ 0.96, 0.96, 1.51 and 1.51 are the protons at H-17, H-16, H-19, H-20 respectively, the signal at δ 5.92 (1H, s) was H-14. The signal at δ 2.43 (1H, dd, $J=7.1, 9.9\text{Hz}$, H-5) indicated that H-5 was β -proton and its structure processed cis-A and B-ring junction. (Jiang B *et al*, 2000) The H-5 related with H-19 could be found from ^1H - ^1H COSY, it was conformed $19-\text{CH}_3$ was at β -position. From the correlation of H-9 and H-7 in ^1H - ^1H COSY, the signal at δ 2.72 (1H, dd, $J=2.2, 2.3\text{Hz}$, H-9) indicated that H-9 was α -configuration, and the signal at δ 4.41 (1H, t, $J=8\text{Hz}$, H-12) indicated that H-12 was at β -position. So, C-12 and C-8 constituted epoxide ring was also β -configuration on C-ring (sp^3 mixed carbon bond angle was 109.5°). All mentioned indicated the C-ring should be boat-form (Fig. 1). Therefore, the chemical structure of compound **1** was concluded to be abiet-13(14)-en-8, 12-epoxy-18-oic acid.

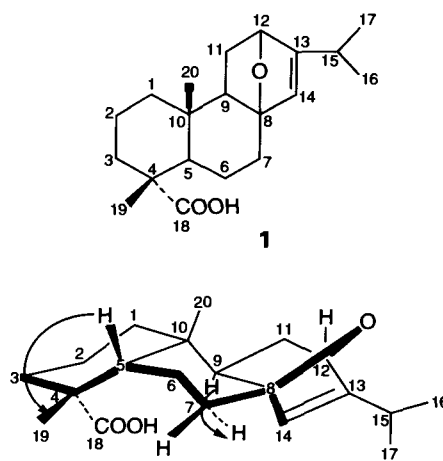


Fig. 1 The key correlations of **1** in ^1H - ^1H COSY

Experimental

General All melting points were measured on an XRC-1 micro melting point apparatus and uncorrected. Optical rotation was taken on a SEPA-300 polarimeter. IR spectral data were measured on a Bio-Rad FTS-135 spectrometer with KBr pellets. MS spectra were recorded on a VG Auto Spec-3000 spectrometer. NMR spectra were run on a Bruker AV-400 and DXB-500 instrument with TMS as internal standard. CC were carried out with silica gel, D101 and TLC silica gel G and silica gel GF254 (Marine Chemical Industry Factory, Qingdao). The spots were visualized by spraying with 20% H_2SO_4 followed by heating.

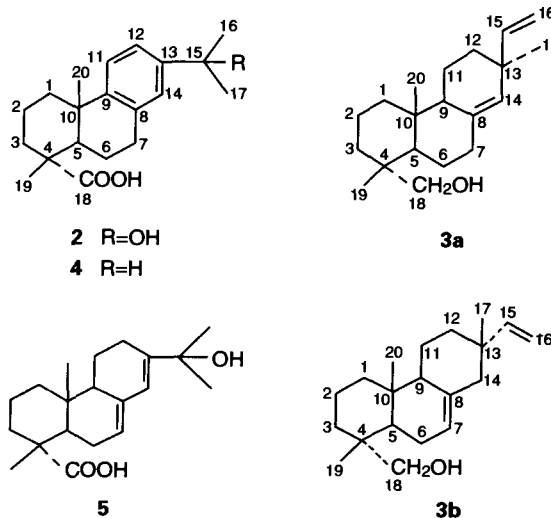


Fig. 2 Structure of compounds **2-5**

Plant material Rosin of *Pinus desiya* var. *langbianensis* was provided by Jingu Forest Industry Company, Jingu county, Yunnan province, China.

Extraction and Isolation The dried and powdered Rosin of *Pinus kesiya* var. *langbianensis* (200g) were purified by repeated column chromatography on silica gel and successively partitionated with petroleum-ester: acetone (10:1, 10:2, 10:5), acetone, MeOH, to yield six compounds **1**, **2**, **3a**, **3b**, **4** and **5**.

Compound **2** (67 mg): $C_{20}H_{28}O_3$, white powder, mp 101–103°C. UV $\lambda_{max}^{CHCl_3}$: 274.5, 266nm. 1H NMR ($CDCl_3$, 400 MHz) δ : 7.09–7.20 (3H, m, H-11, H-12, H-14), 1.00 (3H, s, 4-CH₃), 1.20 (3H, s, 10-CH₃), 1.49 (6H, s, 16, 17-2×CH₃), 2.22 (1H, brd, 3-H α). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ : see Table 2; EI-MS m/z (%): 316 ($[M]^+$ 50%), 301 ($[M-CH_3]^+$ 100%), 283 ($[M-CH_3-H_2O]^+$ 30%), 255 (55%), 197 (60%), 131 (35%), 59 (54%). (Yu and Yang, 1999a).

Table 2 ^{13}C NMR data for the compounds 2–5

No.	2	3a	3b	4	5
1	37.97	38.36	39.25	37.90	38.30
2	16.53	18.14	18.98	18.52	18.03
3	36.78	35.42	35.61	36.72	37.22
4	47.39	37.97	37.53	47.40	46.25
5	44.66	47.45	43.39	44.57	44.88
6	21.73	22.12	23.13	21.74	25.73
7	31.60	35.61	121.20	29.98	122.85
8	134.72	138.14	135.35	134.65	134.68
9	147.85	51.13	51.64	146.74	50.71
10	36.96	38.57	37.17	36.83	34.44
11	124.08	18.98	20.03	124.08	37.94
12	121.98	36.04	37.57	123.86	22.56
13	146.01	35.34	36.71	145.67	144.37
14	124.92	127.66	46.10	126.87	122.53
15	72.04	147.07	150.11	33.44	72.88
16	30.12	112.63	109.06	23.96	28.64
17	30.12	29.32	21.42	23.96	28.64
18	184.32	71.66	78.83	185.19	183.99
19	16.28	18.00	17.78	16.19	16.72
20	25.01	15.60	15.20	25.09	13.95

Compounds **3a** + **3b** (4.37 g): colorless gum. It was the mixture of two compounds (**3a** + **3b**) in the gum. Their molecular formula was $C_{20}H_{32}O$. mp 74°C. UV $\lambda_{max}^{CHCl_3}$: 250.5nm. IR ν_{max}^{KBr} : 3364, 2927, 1638, 1453, 1384, 1040, 998, 912 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ : 0.86 (3H, s, 4-CH₃), 0.98 (3H, s, 10-CH₃), 1.34, 1.48 (2H, m, H-2), 3.10, 3.37 (2H, m, H-18), 4.95 (2H, m, CH₂), 5.12 (1H, m, CH), 5.75 (1H, m, CH). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ : see Table 2. EI-MS m/z (%): 288 ($[M]^+$ 60%), 273 ($[M-CH_3]^+$ 27%), 257 (100%), 241 (12%), 231 (8%), 213 (9%), 199 (18%), 189 (25%), 175 (24%). (Zhang, 1999; Cong and Su, 2000a).

Compound **4** (8.103 g): $C_{20}H_{28}O_2$, white flat crystal, mp 155–160°C. UV $\lambda_{max}^{CHCl_3}$: 255–275nm. IR ν_{max}^{KBr} : 2931, 1692, 1613, 1498, 1461, 1279, 1187, 1133, 1037, 908, 882, 733, 716, 661. 1H NMR ($CDCl_3$, 500 MHz) δ : 7.04–7.22 (3H, m, H-11, H-12, H-14), 1.23 (3H, s, 4-CH₃), 1.31 (3H, s, 10-CH₃), 1.06 (6H, d, 16, 17-2×CH₃), 2.23 (1H, brd, 3-H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ : see Table 2. (+)-FAB-MS m/z (%) 301 ($[M^+]$ 100%), 285 ($[M^+-CH_3]$ 83%), 239 ($[M^+-H_2O-C_2H_4]$ 23%) (Yu and Yang, 1999; Cong and Su, 2000b).

Compound **5** (3.004 g): $C_{20}H_{30}O_3$, white powder in CH_2Cl_2 . mp 87–97°C; UV $\lambda_{max}^{CHCl_3}$: 244.5nm. IR ν_{max}^{KBr} : 3421, 2935, 1696, 1460, 955, 898, 756, 708, 657 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ : 0.80 (3H, s, 4-CH₃), 1.12 (3H, s, CH₃), 1.25 (3H, s, CH₃), 1.52 (3H, s, 10-CH₃), 5.44 (1H, m, 7-H), 6.02 (1H, m, 14-H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ : See Table 2. EI-MS m/z (%) 318 ($[M^+]$ 14%), 300 ($[M-H_2O]^+$ 37%), 283 (11%), 275 (15%), 253 (25%), 237 (32%), 227 (15%), 213 (22%). (Yu and Yang, 1999b; Zhao *et al*, 1999).

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