华南植物学报　1992,试刊 I
BOTANICAL JOURNAL OF SOUTH CHINA

乳突拟耧斗菜中的一新二萜成分

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摘　要

从乳突拟耧斗菜(*Paraquilegia anemonoides*)乙醇提取物的非碱部分中分得两个二萜类化合物：ent-考兰烷-16β,17-二醇和拟耧斗菜素(paraquilegin)。其中拟耧斗菜素是一新化合物,其结构经光谱解析和化学方法证明为 ent-17-咖啡酰氧基-考兰烷-16B-醇。

关键词：乳突拟耧斗菜；二萜；拟耧斗菜素

A NEW DITERPENE FROM *PARAQUILEGIA ANEMONOIDES*

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Abstract

Along with *ent*-kauran-16β, 17-diol, a new diterpene, paraquilegin was isolated from the non-basic fraction of *Paraquilegia anemonoides* and its structure was determined by spectroscopic analysis and chemical correlation.

Key words: *Paraquilegia anemonoides*; Diterpenes; Paraquilegin.

Paraquilegia anemonoides (willd.) Engl. ex Ulbr. (Ranunculaceae) distributed in the northwest of China[1] is used as aborticide by the Tibetan People [2]. Its chemical components were therefore investigated. From the non-basic fraction of its ethanol extract, two diterpenes, *ent*-kauran-16β, 17-diol and paraquilegin (a new compound) were isolated. To our knowledge, non-alkaloidal diterpenes had not been discovered from plants of this family. Here reported is the isolation and the structure elucidation of paraquilegin.

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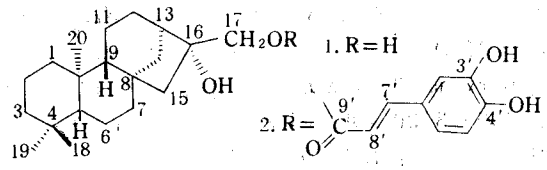

Results and Discussion

Paraquilegin (2) was obtained as light yellow needles. Its molecular formula $C_{29}H_{40}O_5$ was established from MS (M^+=m/z 468), ^1H and ^{13}C NMR (DEPT) spectral data. The IR spectrum showed absorptions for hydroxyl groups (3600—3200cm^{-1}), carbonyl group (1690 cm^{-1}), carbon to carbon double bond (1630 cm^{-1}) and aromatic ring (1600, 1530, 1480 cm^{-1}). The ^1H NMR signals: δ7.52 and 6.22 (each 1H, d, J=16 Hz), 7.03 (1H, d, J=2 Hz), 6.97 (1H, dd, J_1=8 Hz, J_2=2 Hz), 6.76 (1H, d, J=8 Hz), and ^{13}C NMR signals in downfield region from δ 166.7 to δ 113.1 along with EI-MS m/z 163 (100) indicated the presence of a caffeoyl group. When the signals due to the caffeoyl group were removed, the ^1H and ^{13}C NMR data were in good agreement with those of reported *ent*-kauran-16β, 17-diol [3,4], except that the ^{13}C NMR chemical shifts of C-17 and C-16 were downfield by 1.5 ppm and upfield by 2.8 ppm, respectively, suggesting that 17-hydroxyl was esterified. Thus, paraquilegin was determined as *ent*-17-O-caffeolyl-Kauran-16β-ol (2) which was confirmed by the alkaline hydrolysis to give *ent*-kauran-16β, 17-diol and caffeic acid.

Experiment

Melting points were determined on a micro hot-stage and were uncorrected. IR and UV spectra were measured on Analect RFX-65A and Beckman DU-7 spectrophotometers, respectively. Optical rotations were recorded on a Jasco J-20c automatic recording spectropolarimeter. EI-MS were recorded with a Finnigan Incos 50 apparatus at 70 eV. Proton and carbon-13 NMR spectra were measured on a Bruker AM-400 spectrometer with TMS as internal reference. Plant material collected in Gansu Province, China, was identified by Prof. Y. R. Ling, South China Institute of Botany, Academia Sinica. The voucher specimen has been deposited in our department.

1. Extraction and Isolation

The air dried powdered whole plant of *P. anemonoides* (8.5 kg) was extracted with 90% ethanol by cold percolation. The solvent was evaporated *in vacuo* to give a dark brown syrup (250 g). The syrup was stirred with 1000 ml of 2% aqueous sulfuric acid and then extracted with chloroform (1000 ml×3). Removal of chloroform gave a non-basic fraction (100 g). The non-basic fraction was chromatographed on a silica gel column and sequentially eluted with petroleum ether, ethyl acetate and acetone. The residue obtained from ethyl acetate was rechromatographed on a silica gel column, eluted with petroleum ether containing increasing amounts of ethyl acetate (10—40%). The rechromatography gave two crude products which on recrystallization afforded 1 (150 mg) and paraquilegin (110 mg).

2. Identification of Compounds

ent-Kauran-16β, 17-diol: colorless needles (petroleum ether and ethyl acetate); mp 186—189 C; $[\alpha]_D^{18}$ -71 C (c=0.9, MeOH); IR ν_{max}^{KBr} (cm^{-1}): 3400, 1100, 1040; MS m/z (%): 306 (M^+, 0.4), 288 (M^+-H_2O, 2), 275 (M^+-CH_2OH, 100), 257 ($M^+-CH_2OH-H_2O$, 35), 137 (32); ^1H NMR (pyridine-d_5): δ 0.78, 0.83, 0.98 (each 3H, s, H-18, H-19, H-20), 3.98, 4.06 (each 1H, d, J=12 Hz, H-17); ^{13}C NMR data: see Table 1.

Paraquilegin: light yellow needles (EtOAc); mp 246—248 C; $[\alpha]_D^{18}$ -34 C (c=0.04, MeOH); IR ν_{max}^{KBr} (cm^{-1}): 3600—3200 (OH), 1690 (c=0), 1630 (c=c), 1600, 1530, 1480 (aromatic ring); EI-MS m/z (%): 468 (M^+, 2), 450 (M^+-H_2O, 4), 288 (2), 275 (8), 194 (3), 180 (26), 163 (100), 137 (5); ^1H NMR (DMSO-d_6): δ 0.77, 0.82, 0.98 (each 3H, s, H-18, H-19, H-20), 4.15, 4.22 (each 1H, d, J=12 Hz, H-17), 7.52, 6.22 (each 1H, d, J=16 Hz, H-8′ and H-7′), 7.03 (1H, d, J=2 Hz, H-2′), 6.97 (1H, dd, J_1=8 Hz, J_2=2 Hz, H-6′), 6.76 (1H, d, J=8 Hz, H-5′); ^{13}C NMR: see Table 1.

Table 1 ^{13}C NMR Chemical Shifts of Compound 1 and 2[a]

Carbon	2	1	Carbon	2	1
1	41.6 (t)	42.2 (t)[b]	16	78.2 (s)	81.5 (s)
2	18.0 (t)	18.8 (t)	17	67.8 (t)	66.3 (t)
3	41.6 (t)	42.5 (t)[b]	18	33.3 (q)	33.7 (q)
4	32.8 (s)	33.3 (s)	19	21.3 (q)	21.7 (q)
5	56.2 (d)	56.2 (d)	20	17.4 (q)	18.0 (q)
6	20.0 (t)	20.7 (t)	1′	125.7 (s)	
7	36.7 (t)	37.2 (t)	2′	115.7 (d)	
8	44.1 (s)	44.8 (s)	3′	145.5 (s)	
9	55.5 (d)	57.1 (d)	4′	148.5 (s)	
10	39.9 (s)	39.5 (s)	5′	114.1 (d)[c]	
11	17.7 (t)	18.6 (t)	6′	121.1 (d)	
12	26.0 (t)	26.8 (t)	7′	144.9 (d)	
13	45.0 (d)	46.0 (d)	8′	114.6 (d)[c]	
14	39.3 (t)	40.4 (t)	9′	166.7 (s)	
15	52.9 (t)	53.9 (t)			

a) Solvent: pyridine-d_5 for 1, DMSO-d_6 for 2.

b,c) Assignments may be interchanged.

3. Hydrolysis of Paraquilegin

A solution of paraquilegin (30 mg) in 5% KOH/MeOH (5 ml) was allowed to stand at room temperature for 48 hours, and water (5 ml) was then added. The methanol was evaporated *in vacuo*. The aqueous solution was extracted with chloroform (5 ml × 3). The chloroform layer gave a residue which was purified by recrystallization from a mixture of petroleum ether and ethyl acetate (6:4) to afford colourless needles (12 mg). mp 184—187 C; EI-MS and ^1H NMR data were identical with those of 1. The water layer was acidified to pH 3.0 with 2% sulfuric acid. The acidic solution was passed through a tiny MCI gel CHP-20p column first washed with water then eluted with methanol. The methanol elution yielded another hyderolysis product, caffeic acid (5 mg): mp 193—195 C; MS m/z (%): 180 (M^+, 100), 163 (M^+-OH, 55).

Acknowledgements

We thank Prof. Y. R. Ling for botanical identification of *P. anemonoides* and Prof. Baolin Li for EI-MS measurements.

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