Acetonide (**2d**) *of Compound* **2**. Prepared by treatment of **2** with Me_2CO, *p*-toluenesulphonic acid. Colourless oil. EIMS *m/z*: 558 [M^+]. ^1H NMR (400 MHz): δ0.73, 0.94 (each *s*, 3H), 0.95 (*d*, *J* = 6.5 Hz), 1.01, 1.16, 1.23, 1.27 (each *s*, 3H), 1.39, 1.51 (each *s*, 3H, Acetonide diMe), 2.61 (*s*, 1H, H-18), 3.60 (*s*, 3H, -COOMe), 3.58 (*d*, *J* = 4.1 Hz, 1H, H-1 or 3), 3.87 (*d*, *J* = 7.7 Hz, 1H, H-3 or 1), 4.18 (*dd*, *J* = 4.1, 7.7 Hz, 1H, H-2), 5.40 (*br s*, 1H, H-12). Another acetonide (**2e**) was detected by TLC but not identified with the spectral data.

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Phytochemistry, Vol. 27, No. 1, pp. 299–301, 1988.
Printed in Great Britain.

0031-9422/88 $3.00 + 0.00

TRITERPENOIDS FROM *SALVIA PRZEWALSKII*

NING WANG, MASATAKE NIWA* and HOU-WEI LUO

Nanjing College of Pharmacy, Nanjing, China; *Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

(*Revised received* 15 *April* 1987)

Key Word Index—*Salvia przewalskii*; Labiatae; triterpenoids; przewanoic acid A; przewanoic acid B.

Abstract—Oleanolic acid and two novel triterpenoids, przewanoic acid A and przewanoic acid B, were isolated from the dried roots of *Salvia przewalskii*. Their structures were elucidated on the basis of chemical and spectral methods.

INTRODUCTION

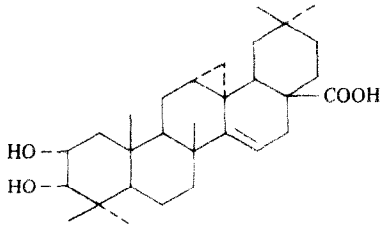
The Tibetian folk drug 'Hong Qin Jiao' is the dried roots of *Salvia przewalskii* Maxim, which is widely distributed in the western areas of China [1–3]. It has been reported that its main chemical components are the *O*-naphthaquinone diterpenes [4, 5]. The present paper describes the isolation and elucidation of two novel triterpenoids, przewanoic acid A and przewanoic acid B, along with a known triterpenoid, oleanolic acid.

RESULTS AND DISCUSSION

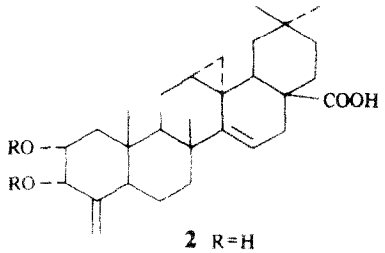
Przewanoic acid A (**1**), white needles, mp 269–270°, $[\alpha]_D$ + 125° had the molecular formula $C_{30}H_{46}O_4$. Its UV spectrum λ_{max}^{MeOH} 211 nm (log ε3.65) showed the probable presence of a double bond conjugated cyclopropane [6]. The ^1H NMR spectrum showed the presence of six methyl groups in agreement with the ^{13}C NMR spectral data (δ17.5, 17.5, 22.2, 22.8, 29.5, 32.6; Table 1). Also the ^1H NMR spectrum revealed one allylic hydrogen and two secondary hydroxyls. The signal at high field (−0.08, *dd*, 1H, *J* = 4.8, 4.8 Hz) is characteristic of the CH_2 in a cyclopropane [6, 7].

The coupling relationships of related protons were assigned from the comparative study of the ^1H–^1H 2D COSY data. The signals at 5.82 (*dd*, 1H, *J* = 7.2, 3.6 Hz), 2.79 (*dd*, 1H, *J* = 13.2, 7.2 Hz) and 2.07 (*dd*, 1H, *J* = 13.2, 3.6 Hz) were a group of corresponding protons. This showed the presence of part structure $^{14}C = {}^{15}CH-{}^{16}CH_2-$. The signals at 4.29 (*ddd*, 1H, *J* = 10.7, 4.0, 2.6 Hz, CHOH) and 3.77 (*d*, 1H, *J* = 2.6 Hz, CHOH) were coupled with each other. This indicated two secondary hydroxy groups which should be placed at C-2 and C-3, respectively, in a *trans*-diaxial configuration ($J_{2H\text{-}3H}$ = 2.6 Hz).

The position of the carboxyl group at C-17 and the double bond at the Δ^{14}-position was established from the mass spectral fragmentation pattern of przewanoic acid A (**1**). Compound **1** exhibited a fragment peak at *m/z* 316 (**1a**). This ion peak was accompanied by a peak 15 mass units lower (**1b**) which was formed by the loss of the allylically activated methyl group at C-8. Moreover, the mass spectrum of **1** showed a peak at *m/z* 232 (**1c**) derived from rings D and E. Furthermore, the fragment **1c** loses the carboxyl substituent at C-17 giving rise to a fragment base peak at *m/z* 187 (**1d**). This type of fragmentation is

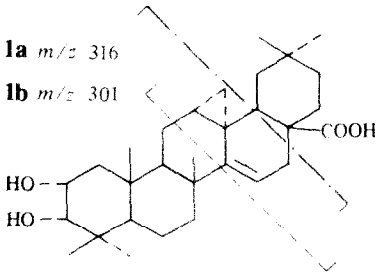


1



2 R=H

3 R=Ac

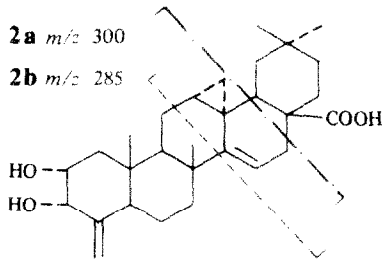


1a *m/z* 316

1b *m/z* 301

1c *m/z* 232

1d *m/z* 187



2a *m/z* 300

2b *m/z* 285

2c *m/z* 232

2d *m/z* 187

consistent with the mass spectral data of Δ^{14}-taraxerene derivatives reported by Djerassi *et al.* [8–10].

From these data the compound **1** was assigned tentatively the structure 2α,3α-dihydroxy-12,13-cyclo-taraxerane-14-en-28-oic acid.

Another triterpenoid, przewanoic acid B (**2**), white needles, mp 258–259°, $[\alpha]_D$ + 103° had the molecular formula $C_{29}H_{42}O_4$. Its spectra are similar to those of compound **1**. However, notable differences between **1** and **2** could be seen with regard to the following points. The ^{1}H NMR spectrum showed the presence of four tertiary methyl groups on saturated carbons at δ 0.72, 0.90, 0.91, 0.96 (each *s* and 3 H). Furthermore, the signals at 5.06 and 4.73 (each *s* and 1 H) showed the presence of an exocyclic methylene group. This was comfirmed by the ^{13}C NMR spectral data at δ 14.5, 22.1, 29.3, 32.3 (each *q*) and 150.2 (*s*), 111.3 (*d*) (Table 1).

The position of the exocyclic methylene at C-4 was established by comparison with the HRMS data of compounds **1** and **2**. The fragment at *m/z* 300.2062 (**2a**, $C_{20}H_{28}O_2$) and 285.1848 (**2b**, $C_{19}H_{25}O_2$, **2a**-Me) resulted from RDA cleavage of ring D and are 16 mass units lower than **1a** and **1b**, respectively. On the other hand, both the fragment peaks at *m/z* 232.1473 (**2c**, $C_{15}H_{20}O_2$) and 187.1462 (**2d**, $C_{14}H_{19}$, **2c**–COOH) resulting from ring C cleavage were the same as **1c** and **1d**. Moreover, the chemical shift value of the 3β-proton moved from δ 3.77 in **1** to 4.18 in **2**, due to the deshielding effect of an exocyclic methylene instead of a geminal dimethyl group.

EXPERIMENTAL

Plant material. The roots of *Salvia przewalskii* Maxim were collected in the Gansu province of China, during the autumn of 1984.

Extraction. The dried roots (10 kg) were extracted with hot 95% EtOH. The residue (203 g) after evapn of solvent was chromatographed on a silica gel column eluted successively with cyclohexane CH_2Cl_2–EtOAc, yielding oleanolic acid (25 mg), przewanoic acid A (18 mg) and przewanoic acid B (42 mg) as well as 12 *O*-naphthaquinone diterpenes.

Przewanoic acid A (**1**). Recrystallized from Me_2CO as white needles, mp 269–270°, $[\alpha]_D$ + 125° (MeOH; *c* 0.08). Found:

Table 1. ^{13}C NMR spectra of compounds **1** and **2** (25 MHz, TMS as int. standard)*

C	1	2	C	1	2
1	42.8 *t*	42.3 *t*	16	31.1 *t*	30.6 *t*
2	66.2 *d*	69.2 *d*	17	52.8 *s*	52.8 *s*
3	79.2 *d*	75.5 *d*	18	34.9 *d*	34.5 *d*
4	38.7 *s*	150.2 *s*	19	38.9 *t*	35.4 *t*
5	48.7 *d*	45.1 *d*	20	29.0 *s*	28.8 *s*
6	19.5 *t*	20.4 *t*	21	34.3 *t*	33.8 *t*
7	35.7 *t*	36.7 *t*	22	31.1 *t*	32.3 *t*
8	38.7 *s*	37.9 *s*	23	29.5 *q*	111.3 *t*
9	48.0 *d*	44.9 *d*	24	17.5 *q*	
10	37.5 *s*	37.2 *s*	25	17.5 *q*	14.5 *q*
11	18.5 *t*	20.1 *t*	26	22.2 *q*	29.3 *q*
12	14.9 *d*	14.6 *d*	27	11.5 *t*	11.3 *t*
13	23.8 *s*	23.4 *s*	28	179.9 *s*	180.9 *s*
14	156.6 *s*	156.4 *s*	29	32.6 *q*	32.3 *q*
15	118.3 *d*	117.8 *d*	30	22.8 *q*	22.1 *q*

*Compound **1** in pyridine, **2** in $CDCl_3$.

$[M^+]$ 470.3485; $C_{30}H_{46}O_4$ requires: 470.3564. UV λ_{Max}^{MeOH} nm (log ε): 211 (3.65). IR ν_{Max}^{KBr} cm^{-1}: 3584, 3384, 1695. ^1H NMR (400 MHz, pyridine-d_5): δ5.82 (*dd*, 1H, J = 7.2, 3.6 Hz), 4.29 (*ddd*, 1H, J = 10.7, 4.0, 2.6 Hz), 3.77 (*d*, 1H, J = 2.6 Hz), 0.86, 0.93, 0.94, 1.04, 1.13, 1.20 (each 3H, *s*), −0.08 (*dd*, 1H, J = 4.8, 4.8 Hz). For ^{13}C NMR, see Table 1. EIMS (70 ev) *m/z* (rel. int.): 470 $[M]^+$ (82.8), 455 $[M-Me]^+$ (7.5), 452 $[M-H_2O]^+$ (90.9), 425 $[M-COOH]^+$ (7.7), 316 (2.1), 301 (30.5), 232 (1.2), 187 (100), 133 (34.2).

Przewanoic acid B (**2**). Recrystallized from MeOH as white needles, mp 258–259°, $[\alpha]_D$ + 103° (MeOH; *c* 0.465). Found: $[M]^+$ 454.3381; $C_{29}H_{42}O_4$ requires: 454.3252. UV λ_{Max}^{MeOH} nm (log ε): 210 (3.65). IR ν_{Max}^{KBr} cm^{-1}: 3426, 1694, 1650, 905. ^1H NMR (400 MHz $CDCl_3$): δ5.58 (*dd*, 1H, J = 7.4, 4.0 Hz), 5.06 (*s*, 1H), 4.73 (*s*, 1H), −0.08 (*dd*, 1H, J = 4.8 Hz). For ^{13}C NMR, see Table 1. EIMS (70 ev) *m/z* (rel. int.): 454 $[M]^+$ (29.1), 439 $[M-Me]^+$ (5.1), 436 $[M-H_2O]^+$ (34.8), 409 $[M-COOH]^+$ (4.5), 300 (8.2), 285 (8.6), 232 (4.1), 187 (100), 133 (22.1).

Przewanoic acid B acetate (**3**). Compound **2** (6 mg) was dissolved in pyridine (0.4 ml) and Ac_2O (0.6 ml) and left overnight. Normal work-up gave przewanoic acid B acetate (4 mg) as needles. ^1H NMR (90 MHz $CDCl_3$): δ1.98 (*s*, 3H, COMe), 2.07 (*s* 3H, COMe).

Acknowledgement—We thank Mr Ji Jiang, Center of Physico-Chemical Tests, for the measurement of mass spectra.

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Phytochemistry, Vol. 27, No. 1, pp. 301–303, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00

MYRIANTHINIC ACID: A NEW TRITERPENOID FROM *MYRIANTHUS ARBOREUS*

F. NGNINZEKO NGOUNOU, DAVID LONTSI and B. LUCAS SONDENGAM*

Department of Organic Chemistry, University of Yaoundé, D.P. 812 Yaoundé, Cameroon.

(*Revised received* 27 *March* 1987)

Key Word Index—*Myrianthus arboreus*; Cecropiaceae; bark; pentacyclic triterpenoids; Myrianthinic acid; 3β,6β-dihydroxyolean-12-en-29-oic acid.

Abstract—A new pentacyclic triterpene acid has been isolated from the stem bark of *Myrianthus arboreus* and its structure has been established as 3β,6β-dihydroxyolean-12-en-29-oic acid and named myrianthinic acid.

INTRODUCTION

Myrianthus arboreus P. Beauv., Cecropiaceae [1] is a small tropical African tree, which grows from Guinea to southern Angola, from southern Sudan to western Tanzania and through Ouganda. The plant is widely used in indigenous medicine: the infusion of bark to treat dysentery; the leaves against heartaches, the accidents during pregnancy and dysmenorrheae; the juice of young leaves against toothaches and bronchitis [2]. Early works on *M. arboreus* reported the isolation of peptide alkaloids from the leaves [3], tormentic acid, 2-acetyl tormentic acid, 3-acetyl tormentic acid and euscaphic acid from the root wood [4, 5], and Myrianthic acid from the same organ [6]. We now report the isolation from the trunk bark of *M. arboreus*, of a new triterpenic acid, myrianthinic acid (**2**) as its methyl ester (**1**).

RESULTS

From the methylated ethyl acetate extracts of ground barks, the methyl ester of myrianthinic acid (**1**) $C_{31}H_{50}O_4$ was obtained which crystallized from methylene chloride as colourless granules, mp 145–147°. The IR spectrum revealed absorptions at ν_{max} 1700 (–COOMe) and 1645 cm^{-1}, and at 3450 and 3525 cm^{-1}, indicative of the presence of two hydroxyl groups. Myrianthinic acid

*Author to whom correspondence should be addressed.