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TWO DITERPENES WITH REARRANGED ABIETANE SKELETONS FROM *ZHUMERIA MAJDAE*

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Key Word Index—*Zhumeria majdae*; Labiatae; root; diterpenoids; rearranged abietane skeletons.

Abstract—From the roots of *Zhumeria majdae*, two new diterpene quinones with rearranged abietane skeletons, 12,16-dideoxy aegyptinone B and 12-deoxy-salvipisone, together with manool have been isolated. The structures have been established from detailed NMR data and other spectroscopic evidence.

INTRODUCTION

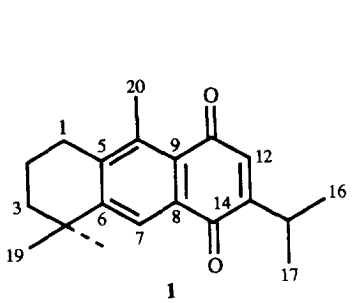
Zhumeria majdae Rech., a newly described plant [1], was first collected by Miss Majda Zhumer in 1966. The plant was subsequently described as the first member of a new genus.

It has a limited geographic range in the southern region of Iran (near the Persian Gulf) where it grows on rather bare rocky slopes. The plant is used by the natives for its pleasant scent and also as a drug [2]. The leaves have been used for many years as a curative for stomach ache, as an antiseptic and for treatment of painful menstruation.

Previous work on the aerial parts showed the presence of linalol and camphor, two flavanoids and a triterpene [3]. It should also be noted that the leaves and flowers by hydrodistillation afforded an unexpectedly large amount of essential oils [4]. As a part of our studies on the diterpenoids from Iranian plants [5–9], we report here on the isolation and structure elucidation of two new diterpene quinones with rearranged abietane skeletons.

RESULTS AND DISCUSSION

The roots of *Z. majdae* contained the coloured diterpenoid quinones (**1**) and (**2**) along with manool (**3**). The red-coloured compound (**1**), *m/z* 296 ($[M]^+$, calc. for $C_{20}H_{24}O_2$) exhibited λ_{max}^{MeOH} nm 263 and 356. The IR spectrum showed absorptions of a 1,4-naphthoquinone (1650, 1635 cm^{-1}) group. The ^1H NMR spectrum (Table 1) showed five methyl signals: three tertiary (including



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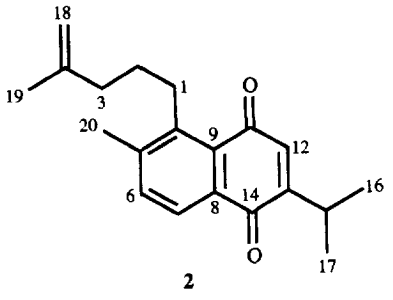

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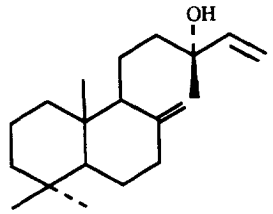

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Table 1. ^{1}H NMR spectral data of compounds 1 and 2 (400 MHz, $CDCl_3$)

H	1	2
1 1′	2.66 *t* (6)	2.99 *br t*, (7)
2 2′	1.84 m	1.61 *br tt* (7,7)
3 3′	1.63 *m*	2.23 *br t* (7)
6	—	7.34 *br d* (8)
7	7.11 *s*	7.02 *d* (8)
12	7.08 *br s*	7.07 *br s*
15	3.01 *br qq* (7, 7)	2.98 *br qq* (7, 7)
16 17	1.14 *d* (7)	1.15 *d* (7)
18 19	1.30 *s*	4.71 *br s* 1.76 *br s*
20	2.55 *s*	2.35 *br s*

Table 2. ^{3}C NMR spectral data of compounds 1 and 2 (100 MHz, $CDCl_3$)

C	1	2
1	19.0 *t*	30.0 *t*
2	28.5 *t*	26.8 *t*
3	37.7 *t*	38.3 *t*
4	34.7 *s*	148.6 *s*
5	144.9 *s*	144.5 *s*
6	153.5 *s*	136.6 *d*
7	126.9 *d*	128.0 *d*
8	133.6 *s*	134.8 *s*
9	126.3 *s*	128.2 *s*
10	144.4 *s*	145.6 *s*
11	182.5 *s*	182.2 *s*
12	140.6 *d*	140.2 *d*
13	138.5 *s*	140.0 *s*
14	182.0 *s*	181.5 *s*
15	26.7 *d*	26.8 *d*
16	21.7 *q*	21.4 *q*
17	21.6 *q*	21.5 *q*
18	31.2 *q*	110.0 *t*
19	31.2 *q*	22.3 *q*
20	16.7 *q*	19.7 *q*

one aromatic) and two secondary. The latter were recognized as a part of an allylic isopropyl group as both signals were coupled with a *br qq* signal at δ3.01 which was sharpened on saturation of the signal at δ7.08. Further decoupling revealed the presence of three successive methylene groups. In the ^{13}C NMR spectrum the chemical shifts of the two most downfield signals at δ182.0 and 182.5 indicated the presence of a quinone. Furthermore, signals for four C=C double bonds were present. Taking into account nine degrees of unsaturation, **1** was a tricyclic compound.

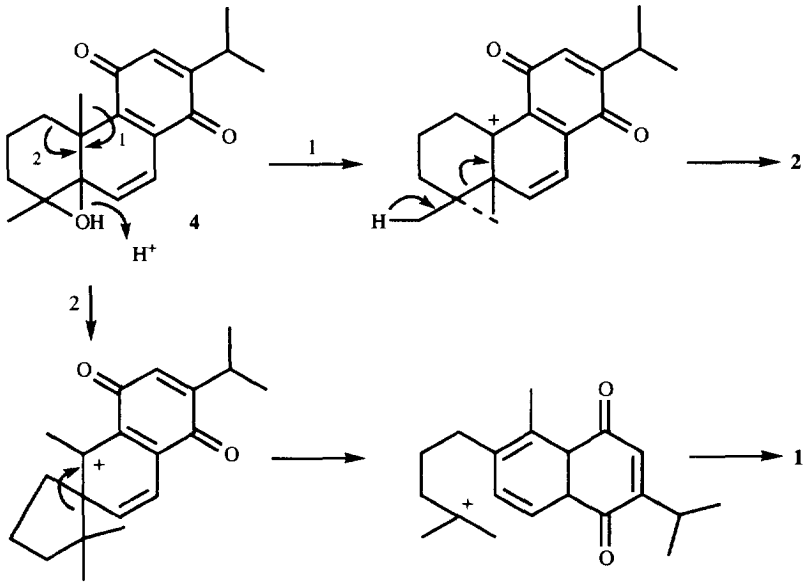
The relative position of the substituents and the connection of the third ring to the naphthoquinone moiety followed from the results of the NOE experiments. The aromatic methyl showed interaction with H-1 and H-1′, while both upfield shifted tertiary methyl groups showed interactions with H-7. The chemical shift of the aromatic methyl is in accordance with a *peri* position to a quinone carbonyl group. Furthermore, the ^{13}C NMR spectrum (Table 2) was also in complete agreement with structure **1** for this new diterpenoid. A similar compound with additional hydroxy groups at C-12 and C-16 named aegyptinone B [10], was described from *Salvia aegyptiaca*. Thus **1** is 12,16-dideoxy-aegyptinone B.

The HR-mass spectrum of **2** showed that it had the same molecular formula ($C_{20}H_{24}O_2$) as compound **1**. While the signals for the quinone part were similar to those of **1** the other signals differed significantly. Two mutually coupled (8 Hz) aromatic signals, an aromatic methyl group and a further substituent complete the structure. The nature of the latter was easily deduced from decoupling experiments. Again NOE difference spectroscopy was helpful for the determination of the relative position of the substituents. In particular, the effects between H-20, H-6 and H-1. Salvipisone, a compound with the same skeleton but having additional hydroxy group at C-12 was obtained from *Salvia aethipis* [11]. The placement of the isopropyl group in both compounds is based on biogenetic consideration. A possible mechanism is presented in Scheme 1. Starting with the abietane derivative **4** (not isolated) methyl and/or alkyl shifts would give **1** and **2**. 2D NMR experiments (^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and HMBC) confirmed the proposed structures and allowed the complete assignment of all ^{1}H and ^{13}C NMR resonances. In particular, some highly diagnostic HMBC correlations were observed for C-14 (H-7 and H-15) in the case of both **1** and **2**, thus confirming the suggested placement of the isopropyl group in each compound.

EXPERIMENTAL

General. NMR: ^{1}H (400 MHz) and ^{13}C (100 MHz), $CDCl_3$, MS: direct inlet, 70 eV. Analytical TLC: aluminium sheets silica gel, 60 F_{254}, layer thickness 0.2 mm, with Et_2O, petrol solvent system, spots visualized under UV light and with ceric sulphate spray reagent; HPLC Li Chrosorb RP-8 (250/10 mm) with MeOH–H_2O mixtures, UV detection.

Plant material. Roots of *Zhumeria majdae* were collected in the south of Iran (near the Persian Gulf). A voucher specimen (L. Z. 277-1) is deposited at the Herbarium of the Department of Botany, Shahid Beheshty University, Tehran, Iran. Dried powdered roots (500 g) were extracted with petrol–Et_2O–MeOH (1:1:1), at room temp. The extract was concd *in vacuo*, weighed and suspended in hot MeOH (10 ml g^{-1} of extract) and then cooled to − 15°. After standing for 4 hr at − 15°, the waxy ppt. was removed by filtration, and the filtrate evapd. *in vacuo*. This yielded a dense oil which was chromatographed on a silica gel column, eluted with petrol (40–60°) containing increasing amounts of Et_2O, 50 ml fractions were collected. Fractions eluted with petrol–Et_2O (1:1) gave 280 mg



Scheme 1. Possible routes for the biosynthesis of **1** and **2** from compound **4**.

of a mixture of **1**–**3**. The mixture were further sepd by prep. TLC and HPLC (MeOH–H_2O, 3:2) to yield **1** (35 mg), **2** (45 mg) and **3** (70 mg).

12,16-*Dideoxy-aegyptinone B* (**1**). Red oil, $[\alpha]_D^{23}$ 0°. ($CHCl_3$; *c* 0.35); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3080 (aromatic), 1650 and 1635 (1,4-naphthoquinone); UV λ_{max}^{MeOH} nm: 263, 356; EI-MS (direct inlet) *m/z* (rel. int.): 296.1776 $[M]^+$ (6), 268 $[M - CO]^+$ (52), 253 $[268 - Me]^+$ (48), 137 (100), 55 (98).

12-*Deoxy-salvipisone* (**2**). Red oil, $[\alpha]_D^{23}$ 0°. ($CHCl_3$; *c* 0.65); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3030, 3010 (aromatic), 3070, 886 (terminal methylene), 1650 and 1635 (1,4-naphthoquinone); UV λ_{max}^{MeOH} nm: 254, 430; EI-MS (direct inlet) *m/z* (rel. int.): 296.1776 $[M]^+$ (18), 240 $[M - C_4H_8]^+$ (90), 225 $[240 - Me]^+$ (50), 200 (100), 185 (55), 183 (40), 69 (35), 55 (43).

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