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Sulfur containing derivatives from *Ferula persica* var. *latisecta*

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Abstract

Two new sulfur containing derivatives, *t*-butyl 3-[(1-methylpropyl)dithio]-2-propenyl malonate (**1**), *t*-butyl 3-[(1-methylthiopropyl)thio]-2-propenyl malonate (**2**) were isolated from the roots of *Ferula persica* Willd. var. *latisecta* D. F. Chamberlain. Their structures were elucidated by spectral methods.

Keywords: *Ferula persica*; Umbelliferae; Sulfur containing derivatives; Roots

1. Introduction

The roots of *Ferula persica* Willd. var. *latisecta* D. F. Chamberlain has been used in folk medicine to treat diabetes (Afifi and Abu-Irmaileh, 2000). Members of the genus *Ferula* are widespread throughout central Asia, specialy in Iran. The chemistry of this genus has been studied by different groups, but only few compounds have been detected in *Ferula persica* (Bagirov et al., 1977; Stetskov et al., 1980).

We now report the isolation and structure elucidation of two new sulfur containing compounds **1** and **2** (Fig. 1) in addition to the coumarins reported previously (Bagirov et al., 1977). It should be pointed out that from the roots of this genus only a few sulfur containing compounds such as asadisulphide (Kajimoto et al., 1989) and rutadisulfides (Al-Said et al., 1996) have been isolated.

2. Results and discussion

Compound **1**, yellow oil, has the formula $C_{14}H_{24}O_4S_2$ (M^+ 320). The UV, ^{1}H NMR and ^{13}C NMR data of **1** were similar with those of asadisulphide (Kajimoto et al., 1989). The IR peak at 1750 cm^{-1} suggested the presence of carbonyl esters, supported by the ^{13}C-signals at δ 170.4, δ 169.7 for two ester groups. The presence of *t*-butyl moiety was demonstrated by a singlet peak at δ 1.53 in ^{1}H NMR spectrum (integrated for 9 protons) and the CH_2 of the allyl ester appeared as a doublet of doublets at δ 4.58 (J = 6.4 Hz, 1.2 Hz). A singlet observed at δ 2.9 was assigned to methylene (CH_2) between two carbonyl group of malonic acid. Two doublet of triplets (*dt*) at δ 5.97 and δ 6.35 for –CH = CH– with one of the coupling constants equal to 14.8 Hz indicated that the double bond is *trans*.

In the ^{13}C NMR spectrum central carbon of *t*-butyl ester and CH_2 of malonate appeared at δ 79.2 and δ 44, respectively and supported by DEPT (Table 1). After comparison of the spectral data of compound **1** and asadisulfide (Kajimoto et al., 1989), we found that part of the ester group, namely the 3-[(1-methylpropyl)-dithio]-2-propenyl group in both molecules is identical and has absorptions in similar positions.

In addition, the mass fragment peaks at *m*/*z* 161 $[CH_3CH_2CH(CH_3)SSCH=CHCH_2]^+$ and *m*/*z* 104 $[SSCH=CHCH_2]^+$ are in accordance with the suggested structure. Complete analysis of IR, UV and ^{13}C NMR spectra led to the proposal of structure **1**.

Compound **2**, yellow oil, has the formula $C_{14}H_{24}O_4S_2$ (M^+ 320). Spectral data of this substance were very similar to those of compound **1**, with only slight differences. The ^{1}H NMR spectrum of compound **2**, was very helpful to identify those differences. In ^{1}H NMR spectrum of compound **2**, methyl protons of SCH_3 appeared as a singlet at δ 2.2 and the CHS proton as a *dd* at δ 3.72. This confirmed our proposal for structure **2**.

Other spectral data of compound **2** are in agreement of the suggested structure and are given in Section 3.

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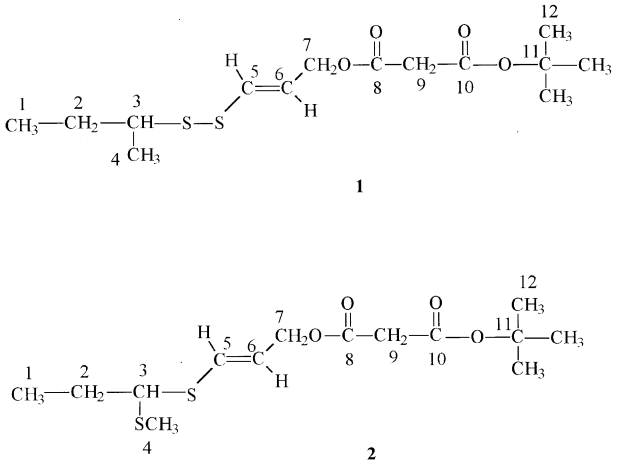

Fig. 1. The structures of compounds **1** and **2**.

Table 1
^{13}C NMR data (100.45 MHz, $CDCl_3$) of compounds **1** and **2**[a]

Number of carbon	**1** $\delta_{(ppm)}$	**2** $\delta_{(ppm)}$	DEPT
1	11.4	11.3	CH_3
2	28.8	27.7	CH_2
3	48	60.5	CH
4	20	14.5	CH_3
5	132.9	132.1	CH
6	122.5	123.4	CH
7	63.7	63.6	CH_2
8	170.4	170.3	C
9	44	43.9	CH_2
10	169.7	169.6	C
11	79.2	79.1	C
12	26.6	26.5	CH_3

[a] All the carbons were assigned with distortionless enhancement by polarization transfer experiment (DEPT).

3. Experimental

UV spectra were recorded on a Shimadzu 160A spectrometer. EIMS were determined on a Finnigan TSQ-MAT 70 at 70 eV. ^1H NMR, ^{13}C NMR and DEPT spectra were measured in $CDCl_3$ as an internal standard using a Varian 400 Unity *plus* spectrometer. FT-IR spectra were recorded on a Nicolet 550 spectrometer. The optical rotation was measured on a Perkin Elmer 241 polarimeter. CC was conducted with silica gel (Kieselgel 60, 0.2–0.5 mm, 35–70 mesh ASTM, Merck, Germany) and TLC with Merck silica gel 60 F_{254} on glass plates.

The plant material was collected in May 2001 from north of Tehran. The plant was identified by the Department of Botany, Faculty of Pharmacy, Tehran University of Medical Sciences (TEH). A voucher speciment (No. 6522) has been deposited at the Herbarium of Faculty of Pharmacy.

Dried powdered roots (500 g) of the plant were extracted with methanol (3.5 l) by maceration for 72 h. The solvent was evaporated and the residue was chromatographed on a silica gel column. Elution with petroleum ether–acetone (10:1) gave a yellow fraction that was further purified by PLC (hexane/EtOAc, 3:1) to yield two yellow oils ($R_f = 0.62$, $R_f = 0.55$ for compounds **1**and **2**, respectively; compound **1** = 280 mg, compound **2** = 67 mg).

t-Butyl 3-[(1-methylpropyl)dithio]-2-propenyl malonate (**1**): Yellow oil, $[\alpha]_D^{25}$: −24.3 ($CHCl_3$, c 2.2), UV ($CHCl_3$): $\lambda_{max} = 250$ nm, IRν_{max}(film) cm^{-1}: 2974, 1750, 1625, 1470, 773. ^1H NMR ($CDCl_3$): $\delta = 0.98$ (*t*, 3H, $J = 7.3$ Hz, MeCH$_2$), 1.3 (*d*, 3H, $J = 6.8$ Hz, MeCH), 1.53 (*s*, 9H, CH_3), 1.51–1.74 (*m*, 2H, MeCH_2CH), 2.8 (*m*, 1H, CHS), 2.9 (*s*, 2H, $COCH_2CO$), 4.58 (*dd*, 2H, $J = 6.4$ Hz, 1.2 Hz, CH_2O), 5.97 (*dt*, 1H, $J = 14.8$ Hz, 6.4 Hz, =CH-CH_2), 6.35 (*dt*, 1H, $J = 14.8$ Hz, 1.2 Hz, SCH=). EIMS: *m*/*z* (%) = 320 (M^+, 100),322 (M + 2, 6), 204 (10), 161 (72), 163 (5), 104 (68), 106 (7), 83 (18). In the ^{13}C NMR spectrum, all carbons were assigned with distortionless enhancement by polarization transfer experiment (DEPT, see Table 1).

t-Butyl 3-[(1-methylthiopropyl)thio]-2-propenyl malonate (**2**): Yellow oil, $[\alpha]_D^{25}$: +27 ($CHCl_3$, c 1.3), UV ($CHCl_3$): $\lambda_{max} = 240$ nm, IRν_{max} (film) cm^{-1}: 2970, 1731, 1362, 1244, 758. ^1H NMR ($CDCl_3$): $\delta = 1.0$ (*t*, 3H, $J = 7.3$ Hz, MeCH$_2$), 1.53 (*s*, 9H, CH3), 1.61–1.79 (*m*, 2H, MeCH_2CH), 2.2 (*s*, 3H, CH_3S), 2.9 (*s*, 2H, $COCH_2CO$), 3.7 (*dd*, 1H, $J = 8.8$ Hz, 5 Hz, CHS), 4.6 (*d*, 2H, $J = 6.4$ Hz, CH_2O), 5.97 (*dt*, 1H, $J = 15.2$, 6.4 Hz, CH=CHCH$_2$), 6.4 (*d*, 1H, $J = 15.2$ Hz, SCH=). EIMS: *m*/*z* (%) = 320 (7), 264 (62), 103 (18), 89 (100), 75 (25). For ^{13}C NMR see Table 1.

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