The structure of linoleic acid ester of *trans*-lachnophyllol isolated from *Aster tataricus*

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Abstract. A linoleic acid ester of an alcohol possessing two triple bonds (*trans*-lachnophyllol) has been isolated from the root of *Aster tataricus*, and its structure determined based on the spectroscopic evidence.

1. Introduction

Aster tataricus L. (Compositae) is widely distributed mainly in Japan, Korea, China, and Mongolia, and its chemical constituents have been extensively studied so far. *A. tataricus*, Japanese name “shion” was first investigated by Nakaoki in 1929 and shionone has been isolated in 1932 [1]. Takahashi’s group as well as Ourisson’s group determined its structure as a tetra-cyclic triterpene ketone [2], whose structure is quite similar to friedelin. We are interested in finding out the derivatives of shionone [2,3], since its congeners are rarely found in nature [4–8], while its backbone-rearranged type triterpenes, namely baccharane-type triterpenoids, have been found in plant kingdom [9–14]. In our continual work on physiologically active compounds in the plant, we have purchased the root of *A. tataricus* produced in China and searched for any other compounds than shionone. However, we could not find triterpenes other than shionone, but found a new linoleic acid ester of acetylenic alcohol **2** as well as its known alcohol **1** [15–18]. Here, we report the details of this new compound.

2. Results and discussion

The MeOH extract of *A. tataricus* was partitioned between EtOAc and water and the EtOAc soluble part was separated by silica gel column chromatography followed by Sephadex LH-20 column chromatography, and finally by HPLC to afford an alcohol **1** and an ester **2**.

The alcohol **1** exhibited a molecular ion peak at m/z 148 and the IR spectrum showed the presence of a hydroxyl group (3500 cm^{-1}), which was confirmed by the ^1H NMR signal at δ 4.24 (2H, dd, $J = 5.1$, 1.8 Hz) as well as the ^{13}C NMR signal at δ 62.6 (CH_2). A double and two triple bonds were revealed

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Fig. 1. Major HMBC correlations of *trans*-lachnophyllol (1).

Fig. 2. 400 MHz HMBC spectrum of compound 2.

by the ^{13}C NMR spectrum (Table 1) as well as the IR spectrum (2250 , 2160 cm^{-1}). The double bond was assigned as *trans* based on the coupling constant ($J = 15\text{ Hz}$). The position of the double and triple bonds were determined by the HMBC spectrum (Fig. 1). Thus, this alcohol was determined as previously known *trans*-lachnophyllol [15–18].

The molecular formula of ester **2** was determined as $\text{C}_{28}\text{H}_{42}\text{O}_2$ by HRMS. The IR spectrum exhibited the presence of an ester (1740 cm^{-1}) and a triple bond (2240 cm^{-1}). The ^1H NMR spectrum was very

Fig. 3. Major HMBC correlations of compound **2**.

Table 1
 ^1H and ^{13}C NMR data for compounds **1** and **2** (in 600 MHz)

No.	1			2			
	$\delta^1\text{H}$	J (Hz)	$\delta^{13}\text{C}$	No.	$\delta^1\text{H}$	J (Hz)	$\delta^{13}\text{C}$
				1	—		173.2
				2	2.32 t	7.70	34.2
				3	1.58 m		24.9
				4	1.31 m		29.6*
				5	1.31 m		29.4*
				6	1.31 m		29.2*
				7	1.31 m		29.1*
				8	2.05 dt	7.0, 6.6	27.2
				9	5.36		127.9
				10	5.36 m		128.1
				11	2.77 t	6.20	25.7
				12	5.36 m		130.1
				13	5.36 m		130.2
				14	2.05 dt	7.0, 6.6	27.2
				15	1.31 m		29.1*
				16	1.31 m		22.6
				17	1.31 m		31.6
				18	0.89 t	7.00	14.1
1	4.24 dd	5.1, 1.8	62.6	1'	4.61 dd	5.9, 1.8	63.5
2	6.36 dt	15.7, 5.1	144.5	2'	6.26 dt	15.8, 5.8	139.3
3	5.78 d	15.7	109.2	3'	5.76 d	15.80	112.2
4	—		72.9	4'	—		72.3
5	—		75.0	5'	—		65.1
6	—		65.1	6'	—		75.8
7	—		84.5	7'	—		85.0
8	2.31 t	7.3	21.7	8'	2.30 t	7.30	21.5
9	1.58 sex	7.3	21.4	9'	1.58 m		21.7
10	1.00 t	7.3	13.4	10'	1.00 t	7.30	13.5

* Assignments may be interchanged.

similar to that of the alcohol **1**, except for the presence of the more olefinic protons and some protons at the higher field. The olefinic protons at δ 6.26 and 5.76 are almost the same ($J = 15$ Hz) as those in **1**, but the methylene protons at δ 4.24 shifted downfield to δ 4.61, suggesting the presence of the ester bond. The proton at δ 4.61 had a correlation peak with the ester carbonyl carbon at δ_C 173.2 in the HMBC spectrum (Figs 2 and 3). The additional four olefinic protons at δ 5.36 should be due to those for olefinic protons of linoleic acid. All other correlations were confirmed by the 2D H-H COSY, HSQC, HMBC, and NOESY spectra. Therefore, compound **2** was established as the linoleic acid ester of the acetylenic alcohol **1**.

This is the first report to find out this ester not only from *A. tataricus* but also from any other source.

3. Experimental

3.1. General

The IR spectra were measured with a JASCO FT/IR-5300 spectrophotometer. The ^1H and ^{13}C NMR spectra were taken with a Varian Unity 200 (200 MHz), Unity 600 (600 MHz), or a JEOL JNM ECP400 (400 MHz) spectrometer. The mass spectra including high-resolution mass spectra were taken with a JEOL JMS AX-500 spectrometer. Chemcopak Nucleosil 50-5 (10×250 mm) was used for HPLC (JASCO pump system). Silica gel 60 (70–230 mesh, Merck) was used for column chromatography and silica gel 60 F₂₅₄ plates (Merck) were used for TLC.

3.2. Plant material

The root of *A. tataricus* L. (9.2 kg) was purchased from China through Josei Pharmacy and Co., Tokushima, Japan.

3.3. Extraction and isolation

Half dried *A. tataricus* (9.2 kg) was pulverized and extracted with MeOH at rt for 3 months. The solvent was evaporated to afford a crude extract (1.8 kg), which was partitioned with AcOEt (82 g) and water. The water layer was extracted with nBuOH (185 g). A part of the EtOAc soluble fraction (27 g) was subjected to SiO₂ column and eluted with CHCl₃–MeOH in gradient. Repeated chromatography of Sephadex LH-20 (CHCl₃–MeOH = 1 : 1), silica gel (hexane–EtOAc and CHCl₃–MeOH, in gradient), and HPLC (hexane–EtOAc, 2%) afforded shionone (164 mg), compound **1** (263 mg) [15–18], and compound **2** (8 mg). **2**: colorless oil; IR (FT) ν_{max} 2240, 1740, 1650 cm^{-1} ; EIMS m/z 410 [M]⁺, 367, 339, 325, 299, 279, 197, 131 (base), 109, 95, 81, and 67; HREIMS m/z 410.3191 [M]⁺ (calcd for C₂₈H₄₂O₂, m/z 410.3185).

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