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POLYACETYLENES FROM *PANAX GINSENG* ROOTS

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Key Word Index—*Panax ginseng*; Araliaceae; roots; C_{17} acetylenes; heptadeca-1-ene-4,6-diyne-3,9,10-triol.

Abstract—Two major and two minor polyacetylenes were isolated from fresh Korean ginseng roots. The chemical structure of the two major polyacetylenes separated were determined by UV, IR, ^{1}H NMR, ^{13}C NMR, mass spectra and elemental analysis. One of them was a new compound identified as heptadeca-1-ene-4,6-diyne-3,9,10-triol.

INTRODUCTION

A polyacetylene compound, panaxynol, from *Panax ginseng* roots was isolated by Takahashi *et al.* in 1964 [1, 2]. The chemical structure of the compound was identical to falcarinol [3] isolated from *Falcaria vulgaris* and carotatoxin isolated from *Daucus carota* [4]. Wrobel *et al.* [5] in 1973 also isolated another type of C_{17} polyacetylene compounds from ginseng.

We now report the isolation of falcarinol and a new polyacetylene compound from fresh ginseng roots and their structural determination.

RESULTS AND DISCUSSION

Four polyacetylenes, A-1–A-3, and B-1, were obtained and each component was examined by UV spectroscopy and compared with published data [6]. The spectra of the separated components showed typical polyacetylene vibrational bands (Table 1). They can be classified into two main polyacetylene groups having two different characteristic UV chromophores, namely a conjugated diyne system for A-1 and B-1 and a conjugated diyne-ene system for A-2 and A-3. Since A-2 and A-3 have higher molar absorption coefficients but show a much smaller absorption peak intensity by HPLC, they exist in minor quantities compared to those of A-1 and B-1. The preparative isolation and physical characterization of A-2 and A-3 were, therefore, not carried out. A-1 was identical to falcarinol by physical characterization.

The molecular skeleton of B-1 was easily recognized by ^{13}C NMR (25.16 MHz, $CDCl_3$) (Table 2). The proton wide band decoupled spectrum of B-1 showed the typical aliphatic methylene carbons at δ 22.2, 31.3, 28.8, 29.0, 26.0 and 27.1, the terminal methyl carbon of the straight aliphatic chain at δ 13.5, the two carbons of the terminal vinyl group at δ 117.3 and 136.3, the allylic carbon to the terminal vinyl group at δ 63.3, and the methylene carbon strongly shielded by conjugated triple bonds at δ 18.9. The resonance of quarternary carbons in the conjugated triple bonds exhibited at δ 77.6, 76.7 and 75.2 in B-1 were not definitely assigned because only three are observed instead of four, one being superimposed with solvent peaks. The ^{13}C chemical shifts of two carbons in B-1, are shifted upfield from δ 126.6 and 122.1 to δ 56.5 and 54.0 as compared to A-1.

The IR of B-1 showed a hydroxyl group at 3400 cm^{-1}, a methylene group at 2940 and 2863 cm^{-1}, conjugated triple bonds at 2260 cm^{-1}, C–O stretching of a secondary hydroxyl group at 1120 cm^{-1}, and a terminal vinyl group at 1000–900 cm^{-1}. Two differences between the spectra of A-1 and B-1 were observed, one being the difference in relative peak intensity at 1120 cm^{-1}, the other being the absence of a peak indicating a *cis* internal double bond at 690 cm^{-1} in spectrum of B-1. The reason for the former is attributed to the presence of additional secondary hydroxyl groups in B-1.

The ^{1}H NMR spectra (79.542 MHz, $CDCl_3$) of B-1 showed a complex spin system of a terminal vinyl group at δ 5.13–6.10, allylic protons to a terminal vinyl group at δ 4.79–4.92, methylene protons of straight hydrocarbon chains at δ 1.28–1.44 and corresponding terminal methyl group protons at δ 0.85. The absence of peaks in the range

Table 1. UV $\lambda_{\max}^{n\text{-hexane}}$ of ginseng polyacetylenes

Component	$\lambda_{\max}$ (nm)	Band spacing (cm^{-1})
A-1	257	2411
	242	1968
	231	2165
	220	—
B-1	254	2297
	240	2193
	228	2223
	217	—
A-2 and A-3	279	2181
	263	1977
	250	2194
	237	2054
	226	3371
	210	—

Table 2. ^{13}C NMR chemical shifts of polyacetylene B-1

Carbon No.	Chemical shifts (δ)
1	117.3
2	136.3
3	63.3
4	77.6
5	76.7
6	75.2
7	—
8	18.9
9	54.0
10	56.5
11	27.1
12	26.0
13	29.0
14	28.8
15	31.3
16	22.2
17	13.5

δ 5.37–5.48 indicates the absence of protons bound to the internal double bond of the aliphatic hydrocarbon chain in contrast to falcarinol. The presence of additional secondary hydroxyl groups in B-1 as compared with A-1 may be responsible for the very complex spin system between δ 1.98 and 3.19 in B-1.

The mass spectra of B-1 determined by EI showed neither an M^+ at m/z 278 nor typical fragment peaks, probably due to its inherent instability. However, the elemental analysis data of B-1 are consistent with the molecular formula $C_{17}H_{26}O_3$.

From these experimental results, B-1 is identified as a C_{17} acetylenic compound differing only in two secondary hydroxyl groups at the 9 and 10 positions instead of the *cis* double bond in falcarinol. B-1 is, thus, heptadeca-1-ene-4,6-diyne-3,9,10-triol. This is a new acetylenic compound among the C_{17} naturally occurring polyacetylenes in Korean ginseng roots. The stereochemistry of the *vic*-diol group is being further pursued.

EXPERIMENTAL

Isolation of heptadeca-1-ene-4,6-diyne-3,9,10-triol. Fresh Korean ginseng roots (*P. ginseng.* A. C. Meyer) 8 kg were finely crushed and extracted with MeOH. MeOH extracts were partitioned between petrol–MeOH (1:1). The petrol layer was washed with 5% NaOH soln several times and the solvent evaporated. The crude oily mixture obtained (4.5 g) was dissolved in the CC solvent (petrol and Et_2O). Stepwise gradient elution from Si gel with petrol–Et_2O (from 5:1 to 2:1) gave two main fractions A (*ca* 120 mg) and B (*ca* 330 mg) containing the polyacetylene compounds. Each fraction separated by CC was further chromatographed by HPLC. To monitor the polyacetylenes from A and B analytical liquid chromatography was performed under the following conditions; column: μ-Bondapak CN (3.9 mm i.d. × 30 cm), solvents: *n*-hexane–CH_2Cl_2(20:1) for fraction A; *n*-hexane–Et_2O(20:1) for fraction B, flow rate: 1.0 ml/min, detector: UV (254 nm). The R_t values (min) were A-1 11.2, A-2 12.0, A-3 14.4 and B-1 8.3.

To isolate the polyacetylenes from each fraction, semi-prep. HPLC was carried out with the same instrument and the same microparticulate column. The polyacetylenes were collected in bottles immersed in dry ice–Me_2CO and covered with Al foil to exclude light. The purity of each separated fraction was rechecked by analytical HPLC. For spectroscopic measurements, the collected fractions were concd by evaporation in a stream of N_2. Residual solvents were removed by rotary vacuum evaporator.

Analysis for B-1 requires for $C_{17}H_{26}O_3$: C, 73.38; H, 9.35; O, 17.27; found: C, 73.06; H, 9.40; O, 17.54%.

The wts of A-1 and B-1 recovered after chromatographic fractionation were 7 and 12 mg, respectively.

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