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Polyacetylene Compounds from *Panax ginseng* C.A. Meyer

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Abstract

Several major polyacetylene compounds were isolated from the petroleum-ether fraction of fresh Korean ginseng roots through solvent fractionation, partition and silica gel column chromatography. Further separation of acetylenic compounds was accomplished by bonded normal phase HPLC utilizing a moderately nonpolar microparticulate column. The preparative separation for the various spectral measurements was carried out by low pressure preparative liquid chromatography. The chemical structure of these polyacetylenes separated was determined by UV, IR/FTIR, ^{1}H NMR, mass spectral and elemental analysis. These are identified to be heptadeca-1-en-4,6-diyn-3,9,10,-triol [1], heptadeca-1,9-dien-4,6-diyn-3-ol, heptadeca-1,8-dien-4,6-diyn-3,10-diol and the 4th was denatured polyacetylene, heptadeca-1,4-dien-6,8-diyn-3,10-diol. Two different p-substituted benzoates of panaxynol were synthesized for the determination of exciton chirality. The circular dichroism spectra in the UV region show that panaxynol p-bromobenzoate and p-dimethylaminobenzoate constitute negative exciton chirality [2]. Isolated major polyacetylene compounds were irradiated in aerated solution with 300 nm UV light to obtain the oxidized product at the allylic alcohol center to corresponding carbonyl compounds such as heptadeca-1-en-4,6-diyn-9,10-diol-3-one and heptadeca-1,9-dien-4,6-diyn-3-one. These photo-oxidation compounds have en-on-diyne chromophore and undergo nucleophilic addition reaction with methanol to yield β-methoxy carbonyl compounds such as heptadeca-9-en-4,6-diyn-1-methoxy-3-one and heptadeca-4,6-diyn-1-methoxy-9,10-diol-3-one.

Introduction

Panax ginseng C.A. Meyer (Araliaceae) had been know for many years as the most valued medicine among all the herbal medicines in Korea, China and Japan. Since the saponin components from American ginseng (*Panax quinquefolium* L.) were isolated by Garriques, the chemical, biochemical, and pharmacological studies on ginseng have been extensively carried out.

Panax ginseng C.A. Meyer has been known to have **about twenty** biologically beneficial activities for human being and it also contains many kinds of chemical principles responsible for the activities. Ginsenosides, in particular, have received the most attention in the study of the biologically active principles of *Panax ginseng* C.A. Meyer.

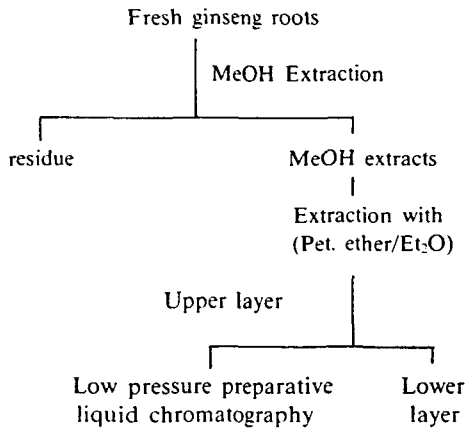
Recently however, it was reported [3,4] that the petroleum ether fraction extracted from Korean ginseng roots inhibits the growth of murine leukemia L5178Y and murine Sarcoma 180 cells *in vitro*, and also **inhibits DNA, RNA and protein synthesis in murine ascitic Sarcoma** 180 cells *in vitro*. The petroleum ether-etheral extracts from ginseng roots contain fatty acids, hydrocarbons, steroids, some polyacetylene compounds, and glycosides. It has not been, however, definitely established which of the components described above shows the cytotoxicity for the carcinoma cells and *Panax ginseng* has been subjected to more systematic studies to determine the chemical components of the root.

A polyacetylene compound from ginseng roots was isolated by Takahashi et al. [5,6]. The chemical structure of the compounds was turned out to be identical with falcarinol [7] isolated from *Falcaria vulgaris* B and Carotatoxin isolated from *Daucus carota* L. [8]. Wrobel et al. [9] also isolated another type of C_{17} polyacetylene compounds from ginseng. The clear spectral data or definite chemical structure of polyacetylenes from ginseng, however, are not unequivocally established at present due to the thermal and photochemical unstability of the naturally occurring polyacetylene compounds and difficulty to isolate large enough quantities necessary for characterization because of the minute concentration of the compound in the ginseng roots.

We have therefore isolated several major polyacetylenes from the fresh ginseng roots and determined their chemical structure and absolute stereochemistry of the chiral center. Thermal and photochemical reactions of the compounds have also been carried out.

Results and Discussion

Freshly prepared petroleum ether/etheral extracts of the *Panax ginseng* C.A. Meyer were subjected to silica gel column chromatography. Several major polyacetylenic compounds were obtained following the scheme shown below. Since the isolation schemes following the classical chromatography and separation techniques such as solvent partition have many problems due to the unstability and due to the minute quantities of samples, complete separation of polyacetylene compounds was accomplished by HPLC system utilizing a bonded normal phase column having moderately low polarity.



Four polyacetylenes, A-1, A-2, A-3 and B-1 were obtained and each component was tested by the UV spectra and compared with the previously published UV data [10]. The UV spectra of separated components show the typical polyacetylene vibrational bands (Table 1). They can be classified into two main polyacetylenic groups having two different characteristic UV chromophore, namely, system with two conjugated triple bonds for A-1 and B-1 components and diyn-ene system with conjugated two triple bonds and one double bond for A-2 and A-3 components. Since A-2 and A-3 components have higher molar absorption coefficients at 254 nm but show smaller peak intensity on the liquid chromatogram than A-1 and B-1 polyacetylenes, they must exist in much smaller quantities than A-1 and B-1.

Table 1. UV λ_{max} of Ginseng Polyacetylenes

Component	λ_{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	279	2181
&	263	1977
A-3	250	2194
	237	2054
	226	3371
	210	

Table 2. ^{13}C NMR chemical shifts of ginseng polyacetylenes

Carbon Number	Chemical Shifts (ppm)			
	A-1	B-1	A-2	A-3
1	117.2	117.3	117.8	118.0
2	136.4	136.3	136.8	136.6
3	63.4	63.3	64.3	64.4
4	79.8	76.6	81.3	146.7
5	70.9	70.7	71.0	112.5
6	63.7	66.3	----	71.5
7	74.1	75.1	74.2	74.9
8	19.3	18.9	108.8	81.5
9	122.1	54.0	150.6	----
10	126.6	56.5	72.8	86.8
11	26.8	27.1	37.6	32.9
12	26.0	26.0	25.9	25.8
13	28.8	29.0	29.9	30.1
14	28.7	28.8	30.1	29.8
15	31.4	31.3	32.5	32.4
16	22.2	22.2	23.3	23.3
17	13.6	13.5	14.7	14.7

The molecular skeleton of each polyacetylene was easily recognized by the use of ^{13}C NMR (50.32 MHz, $CDCl_3$) (Table 2). The proton wide band decoupled ^{13}C NMR spectra of A-1 polyacetylene show the typical aliphatic methylene carbons at 22.2, 31.4, 28.7, 28.8, 26.0 and 26.8 ppm, terminal methyl carbon of the straight aliphatic chain at 13.6 ppm, two carbons of terminal vinyl group at 117.2 and 136.4 ppm, carbon of allylic position to terminal vinyl group at 63.4 ppm, methylene carbon strongly shielded by conjugated triple bonds at 19.3 ppm, and two carbons of internal double bond at 122.1 and 126.6 ppm, carbons of conjugated two triple bonds at 79.8, 70.9, 63.7 and 74.1 ppm. The ^{13}C NMR spectra of B-1 show upfield shift of two carbons, from 126.6 and 122.1 ppm to 56.5 and 54.0 ppm compared to A-1. From the ^{13}C NMR spectral analysis, it is clear that both A-1 and B-1 polyacetylenes have the similar molecular skeletons and functional groups with minor differences.

The infrared spectra of A-1 show hydroxyl group at 3400 cm^{-1}, methylene group at 2940 and 2863 cm^{-1}, conjugated triple bonds at 2260 cm^{-1}, C-O stretching of secondary hydroxyl group at 1120 cm^{-1}, terminal vinyl group at 1000-900 cm^{-1} and internal double bond of cis configuration at 690 cm^{-1}. Those of B-1 show also the same absorption bands at 3400 cm^{-1}, 2940 cm^{-1}, 2863 cm^{-1}, 2260 cm^{-1}, 1120 cm^{-1}, and 1000-900 cm^{-1} as the A-1 spectra. Two differences between A-1 and B-1 spectra were observed, one being the difference of the relative peak intensity at 1120 cm^{-1} and the other the absence of peak at 690 cm^{-1} in the B-1 spectra. The reason of the former difference is attributed to the presence of more secondary hydroxyl groups in B-1 than in A-1 polyacetylene.

The ^1H NMR spectra of A-1 polyacetylene taken in chloroform-d show complex spin system of terminal vinyl group at 5.14-6.13 ppm, protons of internal double bond at 5.37-5.48 ppm, allylic protons to terminal vinyl group at 4.80-4.96 ppm, two allylic protons of internal double bond connected to a hydrocarbon chain at 1.83-2.06 ppm, methylene protons of straight hydrocarbon chains at 1.26 ppm, terminal methyl group protons of aliphatic hydrocarbon chain at 0.87 ppm, and two broad proton doublets at 2.97-3.03 ppm (J=5Hz) indicating an isolated methylene group adjacent to triple bonds and a *cis* double bond. The same pattern of these absorption peaks was found in another isolated C_{17} polyacetylenes having -(C≡C)$_2$-CH_2-CH=CH-*(cis)* group [11,12]. The ^1H NMR spectra of B-1 polyacetylene show the same functional groups as A-1 polyacetylene and show the proton peaks at 5.13-6.10 ppm, 4.79-4.92 ppm, 1.28-1.44 ppm and 0.85 ppm. However, the absence of peaks at 5.37-5.48 ppm range indicates the absence of protons bound to the internal double bond of aliphatic hydrocarbon chains. The presence of more secondary hydroxyl groups in B-1 than A-1 polyacetylene may have caused the very complex spin system in the range of 1.98-3.19 ppm in B-1.

The mass spectra of A-1 polyacetylene determined by the electron impact method show the molecular ion peak at 244, M^+-C_6H_{13} peak by allylic fission [13,14] at 159, but those of B-1 polyacetylene neither show the molecular ion peak at 278 nor the typical fragment peak probably due to the highly unstable property of the B-1 polyacetylene. However, the elemental analysis data of B-1 poly-

acetylene are consistent with the molecular formula $C_{17}H_{26}O_3$.

From these experimental results, it is concluded that the A-1 polyacetylene is heptadeca-1,9-dien-4,6-diyn-3-ol which have the identical spectral data compared with the literature value of the previously isolated panaxynol or falcarinol [6,7] and the B-1 polyacetylene is identified as a C_{17} acetylenic compound A-1 differing only in two secondary hydroxyl groups at 9,10 positions instead of the *cis* double bond in A-1 polyacetylene. The polyacetylene B-1 is thus assigned to be heptadeca-1-en-4,6-diyn-3,9,10-triol. This is a newly found acetylenic compound among the C_{17} naturally occurring polyacetylenes in Korean ginseng roots.

The structure of A-2 and A-3 was determined by the same method The infrared spectra of A-2 show hydroxyl group at 3356 cm^{-1}, methylene group at 2925 and 2854 cm^{-1}, conjugated triple bonds at 2234 cm^{-1}, C-O stretching of secondary hydroxyl group at 1129 cm^{-1}, terminal vinyl group at 1000-900 cm^{-1} and internal double bond of trans conjugation at 955 cm^{-1}. Those of A-3 show also the same absorption bands at 3317 cm^{-1}, 2928 cm^{-1} and 2857 cm^{-1} 2211 cm^{-1}, 1093 cm^{-1}, 1000-900 cm^{-1} and 954 cm^{-1}

The ^1H NMR spectra of A-2 and A-3 show complex spin system of terminal vinyl group at 5.16-5.97 ppm, protons of internal double bond at 5.66-6.32 ppm and 5.68-6.24 ppm, proton attached to secondary hydroxyl group at 4.90 and 4.11 ppm, 4.93 and 4.33 ppm, methylene protons of straight hydrocarbon chains at 1.0-1.5, and terminal methyl protons at 0.88 ppm.

Mass spectra of A-2 and A-3 polyacetylenes do not show molecular ion peaks at 260, but A-2 shows the fragment ion peak at 161 probably due to allylic fission.

Since the C_{17} polyacetylenes isolated have a secondary allylic alcohol functionality, they have a chiral center at C_3 position. In order to investigate this chiral center, two para-benzoate derivatives of panaxynol were prepared and subjected to a circular dichroic exciton chirality method. This method induces the chiral interaction between two isolated but spatially close chromophores, which give rise to Davydov-split Cotton effects. This exciton chirality method is based on the coupled oscillator theory and the polarizability theory [15,16].

The UV spectra of panaxynol p-bromobenzoate and p-dimethylaminobenzoate taken in methanol show λ_{max} at 244 nm and 313 nm respectively. The p-substituted benzoate chromophore exhibits and allowed π-π^* intramolecular charge-transfer band (^1L_a), while the C=C double bond chromophore shows an allowed π-π^* transition at around 195 nm. If the two long axes of benzoate and double bond chromophores constitute a positive exciton chirality, that is, right handed screwness, the Cotton effect at ^1L_a band is positive. On the other hand, if the allyl benzoate constitutes a negative exciton chirality, ^1L_a benzoate Cotton effect should be negative.

Table 3. Molar Circular Dichroism of Benzoates

	p-bromobenzoate	p-dimethylaminobenzoate
λ_{ext}(nm)	244	313
$\Delta\varepsilon$	-4.76	-4.45

The circular dichroism spectra of panaxynol, p-bromobenzoate and p-dimethylaminobenzoate in methanol were taken and the ellipticity obtained from the spectra was transformed into molar circular dichroism as shown in Table 3. Since the value of molar circular dichroism of two benzoates was negative, the secondary allyl benzoates constitute negative exciton chirality and C_3 of panaxynol has the absolute stereochemistry of S configuration.

zoates constitute negative exciton chirality and C_3 of panaxynol has the absolute stereochemistry of S configuration.

When aerated solution of polyacetylenes was irradiated with 313 nm UV light, allylic alcohol center was oxidized to corresponding carbonyl compounds. Thermal oxidation with pyridinium chlorochromate yields the same products.

The carbonyl compounds formed, vinyl ketones, added methanol very readily giving β-methoxy carbonyl compounds. The structures of all the polyacetylenes isolated are summarized.

Preliminary test for cytotoxic activity of a polyacetylene, heptadeca-1-en-4,6-diyn-3,9,10-triol showed much stronger activity than the crude petroleum ether extracts against human carcinoma cells, HRT-18 and HT-29, as shown in the next figure.

Experimental : The six years old fresh ginseng roots were used for these experiments. Solvents for HPLC were HPLC grade n-hexane, ethyl ether and methylene chloride distilled in glass (Burdick and Jackson Lab. Inc.) and filtered through membrane filter (0.45 μm) prior to use. Kiesel gel 60 GF_{254} for thin layer chromatography and Kiesel gel 60 for silica gel column chromatography (70-230 mesh ASTM) were also used.

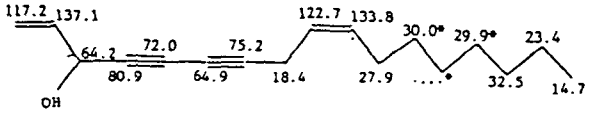
Heptadeca-1,9-diene-4,6-diyn-3-ol

460 mg/1kg (dry weight)

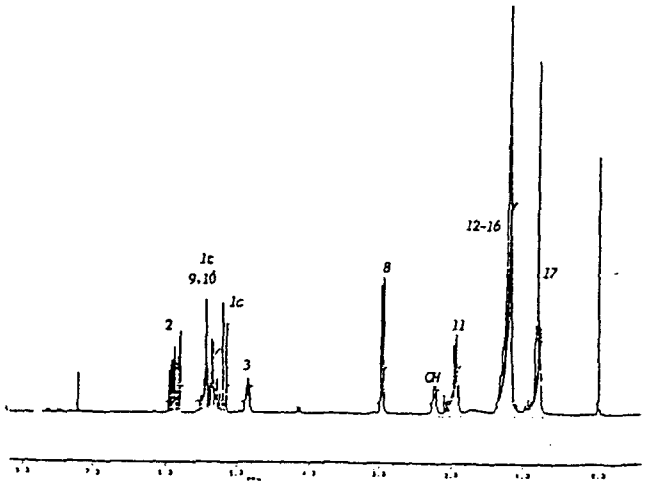
UV (MeOH) : λ_{max}(nm) : 257, 242, 231, 220

IR (NaCL) : $\bar{\nu}$(cm^{-1}) : 3400 (-OH), 2260 (-C≡C-)

MaSS (EI) : 244 $[M]^+$ 159 $[M-C_5H_{13}O]^+$



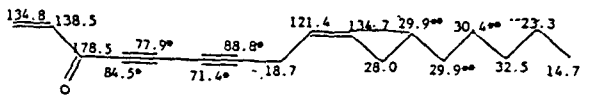
Structure and ^{13}C-NMR Data



^1H-NMR Spectrum

Heptadeca-1,9-dien-4,6-diyn-3-one

UV (MeOH) : λ_{max}(nm) : 291, 274, 260, 246
IR (NaCL) : $\bar{\nu}$(cm^{-1}) : 1655 (-C=O), 2240 (-C≡C-)
MaSS (EI) : No M^{+} peak



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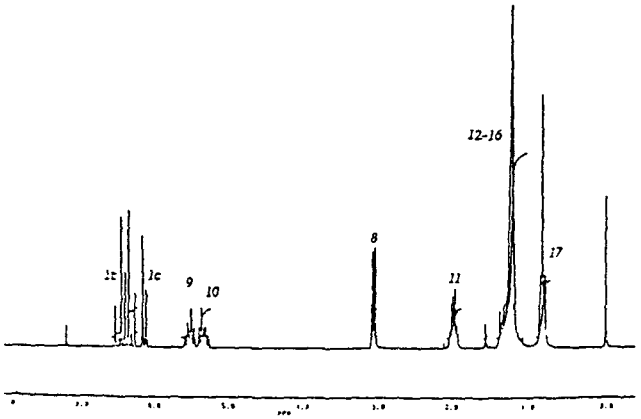
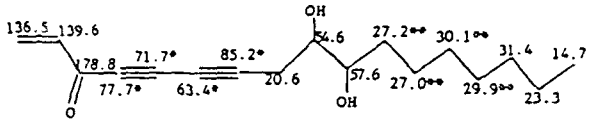


^{1}H-NMR Spectrum

Heptadeca-1-en,-4,6-diyn-9,10-diol-3-one

UV (MeOH) : λ_{max}(nm) : 290, 273, 258, 244
IR (NaCL) : $\bar{\nu}$(cm^{-1}) : 1655 (-C=O), 2240 (-C≡C-)
MaSS (EI) : 258 [M-H$_2$O]$^{+}$



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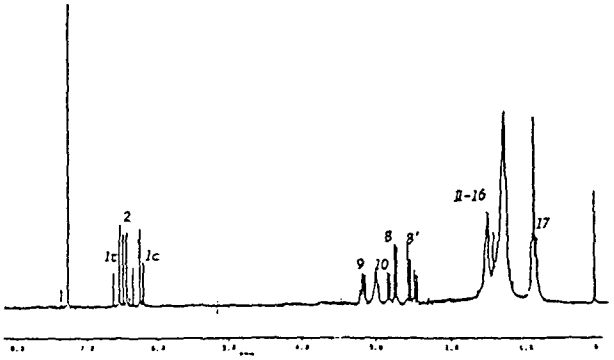
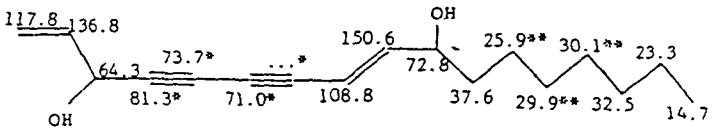


^{1}H-NMR Spectrum

Hetadeca-1,8-dien-4,6-diyn-3,10-diol

80 mg/1kg (dry weight)

UV (MeOH) : λ_{max}(nm) : 283, 268, 253, 238, 226
IR (NaCL) : $\bar{\nu}$(cm^{-1}) : 3359 (-OH), 2234 (-C≡C-)
MaSS (EI) : No M^{+}, 161 [$C_{10}H_9O_2$]$^{+}$
Elemental Anal. ($C_{17}H_{24}O_2$): Found: C, 78.18, H, 9.34
Requires:C, 78.47, H, 9.23

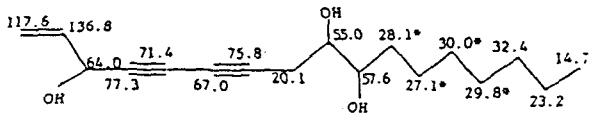


Structure and ^{13}C-NMR Data

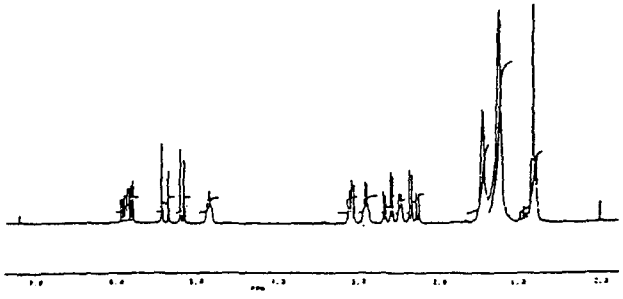
Heptadeca-1-en-4,6-diyn-3,9,10-triol

890 mg/1kg (dry weight)

UV (MeOH) : λ_{max}(nm) : 254, 240, 228, 217
IR (NaCL) : $\bar{\nu}$(cm^{-1}) : 3400 (-OH), 2260 (-C≡C-)
MaSS (EI) : 260 [M-H$_2$O]$^{+}$, 119 [C_9H$_9$O]$^{+}$



Structure and ^{13}C-NMR Data



^{1}H-NMR Spectrum

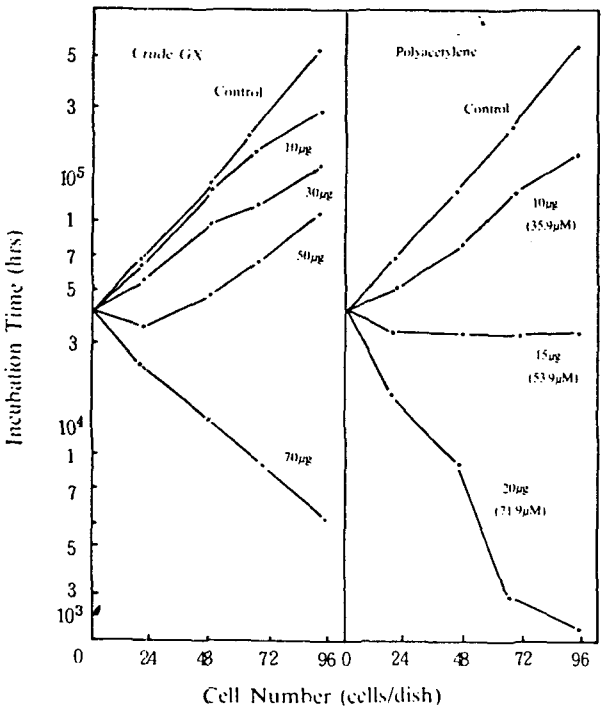


Fig. 1. Growth curves of HRT-18 cells in the culture medium containing various amounts of crude ginseng extract and polyacetylene.

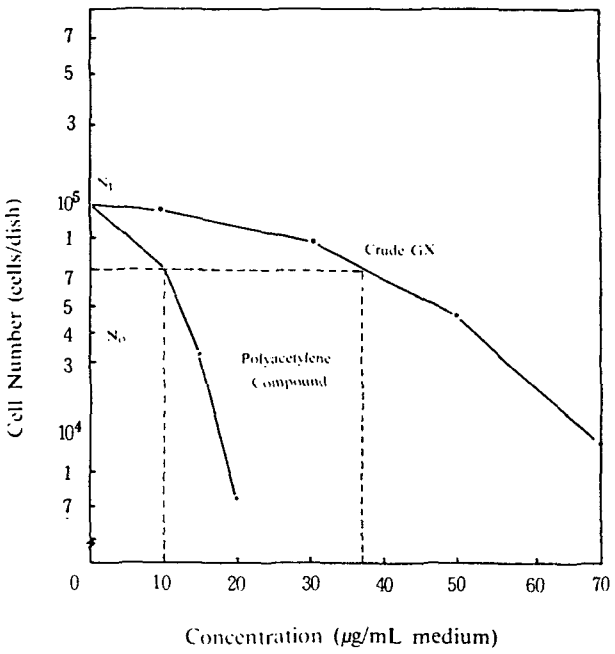


Fig. 2. Dose response curve of crude ginseng extract and polyacetylene on the growth of HRT-18 cells after 48 hours of incubation.

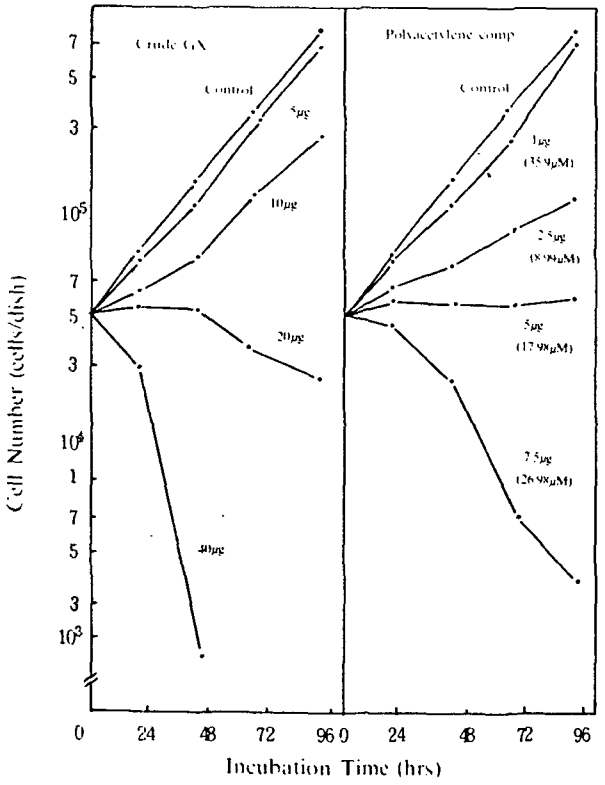


Fig. 3. Growth curves of HT-29 cells in the culture medium containing various amounts of crude ginseng extract and polyacetylene.

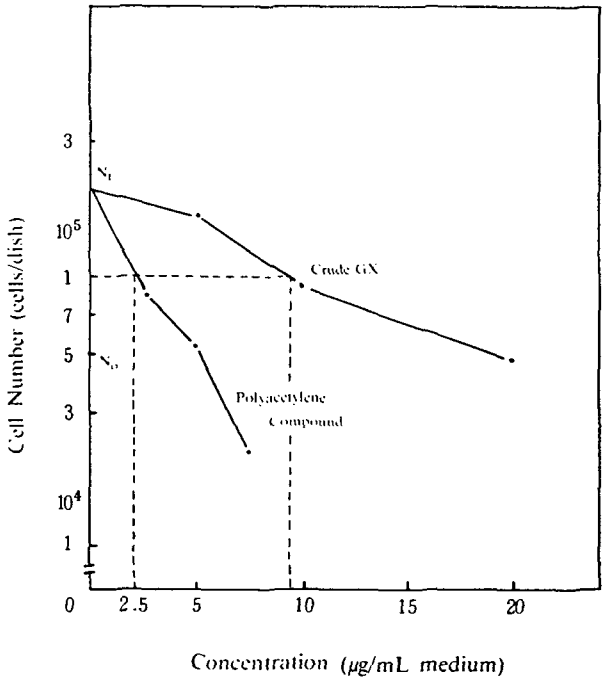


Fig. 4. Dose response curve of crude ginseng extract and polyacetylene on the growth of HT-29 cells after 48 hours of incubation.

Ultraviolet absorption spectra were recorded with a Cary 17 spectrophotometer. Infrared spectra were recorded on a Perkin Elmer 283 B grating spectrometer as neat liquid samples using sodium chloride windows. Pulsed proton NMR spectra were run on a Varian FT-80 A NMR spectrometer at 79.542 MHz and Brucker AM 200 NMR spectrometer at 200 MHz utilizing chloroform-d solvent as internal lock signal. Carbon-13 NMR spectra were run on a Varian FT-80A NMR spectrometer (20.00 MHz) and Brucker AM 200 NMR spectrometer (50.32 MHz) at ambient temperature. Mass spectra were determined with a JEOL DX-300 GC/MS (low resolution) system through electron impact method. Circular dichroism spectra were recorded with a JASCO J-20 Spectrophotopolarimeter.

Isolation of Polyacetylene Compounds : Fresh Korea ginseng roots (8 kg) were finely crushed up and extracted with methanol. Methanolic extracts were partitioned in the mixed solvents of petroleum ether-ethyl ether (1:1). Petroleum ether layer was washed with 5% NaOH solution several times. After the solvent of the petroleum ether layer was evaporated, a crude oily mixture (4.5 g) was dissolved in column chromatographic solvents (mixed solvents of petroleum ether and ethyl ether) for silica gel column chromatography. Stepwise gradient elution with petroleum ether/ethyl ether varying the solvent polarity (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 column chromatography was further chromatographed by an Waters Associates Model 244 HPLC. To monitor the polyacetylenes A and B analytical liquid chromatography was performed under the following conditions : column : μ-Bondapak CN (3.9 mm ID × 30 cm), solvent : n-hexane-CH_2Cl_2 (20 : 1) for A fraction ; n-hexane-Et_2O (20:1) for B fraction, 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 each polyacetylene from each fraction, semi-preparative HPLC was carried out with the same instruments and the same microparticulate column. The polyacetylenes were collected in bottles immersed in dry ice-acetone and covered with aluminum foil to exclude light. The purity of each separated fraction was rechecked by analytical PHLC. For spectroscopic measurements, collected fractions were concentrated by bubbling the purified nitrogen gas to evaporate off the solents. Residual solvents were removed by rotary vacuum evaporator. Anal. for B-1 Cacld : 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. For A-2 Cacld : for $C_{17}H_{24}O_2$: C, 78.47 ; H, 9.23 ; O, 12.30. Found : C, 78.17 ; H, 9.34 ; O, 12.48. For A-3 Cacld : for $C_{17}H_{24}O_2$: C, 78.47 ; H, 9.23, O, 12.30. Found : C, 78.76 ; H, 9.18 ; O, 12.06.

p-Substituted Benzoates Formation of Panaxynol : To a stirred solution of 0.24 mmol two p-substituted benzoic acid (p-bromo and p-dimetylamino) in 1 ml anhydrous methylene chloride was added 1-2 mg 4-(dimethylamino) pyridine as a catalyst and 0.08 mmol. heptadeca-1,9-dien-4,6-diyn-3-ol, 1.5 molar equivalents of dicyclohexylcarbodiimide were added to the reaction mixture at 0°C, which was then stirred for 5 min. at 0°C and 4 hours at room temperature. Precipitated urea was then filtered off and the filtrate dissolved in methylene chloride was treated with Seppak silica cartridge (Waters Associates). Thus obtained methylene chloride solution was washed twice with 0.5 N HCl and with saturated sodium bicarbonate solution, and dried over magnesium sulfate. Two p-substituted benzoates were analyzed by silica gel TLC and HPLC, and separated by semi-preparative liquid chromatography.

Two panaxynol benzoates dissolved in methanol were used for measurements of circular dichroism spectra in UV region.

Irradiation of Heptadeca-1-en-4,6-Diyn-3,9,10-Triol : About 10 mg of heptadeca-1-en-4,6-diyn-3,9,10-triol dissolved in nondegassed 15 ml liquid chromatography solvents (n-hexane/ether) were irradiated in a Rayonet Photochemical Reactor Model RPR-208 equipped with 254 nm mercury arc lamps or 300 nm fluorescent lamps (The Southern New England Ultraviolet Company). The irradiation times were 20 minutes under 254 nm UV light and 10 hours under 300 nm UV light. After the irradiation, the resulting photoreaction mixtures were concentrated by bubbling of nitrogen gas, and analysis by HPLC and the product was isolated by semi-preparative HPLC. The same procedures were followed in the photooxidation of other polyacetylenes.

Thermal Oxidation of Heptadeca-1-en-4,6-Dyin-3,9,10-Triol : The pure heptadeca-1-en-4,6-diyn-3,9,10-triol (3×10^{-4}M) was added in one protion with stirring to a four fold excess of 4-(dimethylamino) pyridinium chlorochromate or manganese dioxide in methylene chloride solution (10 ml). After stirring for 15 hours, the mixture was diluted with petroleum ether. The resulting solution was passed through a Sepak cartridge (silica), and the reaction product was analyzed by UV and HPLC.

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인삼의 Polyacetylene 화합물

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폴리아세칠렌계 화합물이 함유된 인삼의 석유 에텔 추출물은 시험관내 실험에서 Sarcoma 180, Walker carcinosarcoma 256, L_{1210}leukemic lympocyte의 성장을 억제한다. 우리는 석유 ether 추출물로 부터 몇가지 포리아세틸렌계 화합물을 분리하여 화학구조를 밝혔다. UV, IR ^{1}H NMR, ^{13}C NMR, EI mass, CI mass, 원소분석과 산화 또는 산촉매 가수분해와 같은 화학적인 방법으로 얻어진 자료에 근거하여 이들은 heptadeca-1,9-dien-4,6-diyn-3-ol, heptadeca-1-en-4,6-diyn-9,10-epoxy-3-ol 및 heptadeca-1,8-dien-4,6-diyn-3,10-diol 로 밝혀 졌다.