

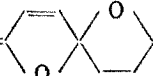
Polyacetylenic Compounds from Chrysanthemum Sibiricum Fischer. Part I.

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〈Abstract〉

The polyacetylene contents of Chrysanthemum Sibiricum Fischer have been examined. Their isolation, characterization and structure determination are described. They are the C₁₃ Spiroketalenoethers, cis and trans $H_3C-(C\equiv C)_2-CH=$  and C₁₆ Triyne-diene acetate $H_3C-(C\equiv C)_3-(CH=CH)_2-(CH_2)_3-OAc$.
t, t

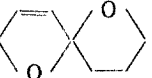
구절초 속에 들어있는 폴리아세틸렌 화합물에 관한 연구(제 1 보)

안정수 · Harry Heaney* · 이태영**

화 학 과

(1985. 4. 30 접수)

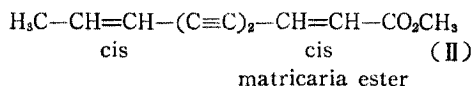
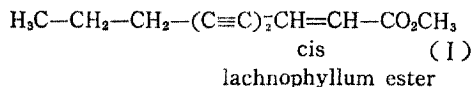
〈요 약〉

한국산 구절초로부터 세가지 폴리아세틸렌성분을 추출, 분리하여 그 구조식을 밝혔다. 그 화합물들의 구조는 C₁₃의 cis와 trans의 Spiroketalenol ether: $H_3C-(C\equiv C)_2-CH=$  와 C₁₆의 Triyne-diene: $H_3C-(C\equiv C)_3-(CH=CH)_2-(CH_2)_3-OAc$ 임을 알았다.
t, t

I. Introduction

In 1936, Russian workers(W. W. Wiljams et al)¹ characterized the first natural diacetylene, the lachnophyllum ester(I), isolated from the essential oil of Lachnophyllum gossypinum Bge. N. A. Sorensen and his Co-workers² isolated a further diacetylenic ester(II) from the may-

weed-Matricaria inodora L. -the matricaria ester in 1941.



When new methods of structure determination became available, the natural acetylenes gave

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rise to a new large group of natural products. Around 1950, F. Bohlmann and his coworkers and E.R.H. Jones and his coworkers started their work on synthesis and spectroscopy of polyacetylenes. Knowing the spectral regularities, the number of known new acetylenes increased rapidly in the following years and several reviews on this subject have already been written.³⁻⁹

No published reports were found in the literature pertaining to the polyacetylenic contents of *Chrysanthemum Sibiricum* Fischer, generally known in Korea as a herb medicine for peptic, tonic, and neuralgia¹⁰⁻¹¹. In this paper we wish to describe the structures of three acetylene compounds, extracts of *Chrysanthemum Sibiricum* F. No attempts were made to determine the structure of those compounds which occurred in small amounts and could almost certainly be identified as known polyacetylenes on the basis of their U.V. and I.R. Spectra.

We plan to report in more detail later, on the mass spectra and C¹³N.M.R. spectra of polyacetylenic compounds as well as to extend the study to other polyacetylenes in small amount.

II. Experimental

1. Plant material

Chrysanthemum Sibiricum F. was obtained from the Kyung-dong Market. The plant grown at Kwang-Nung, Kyung-gi-do province in Korea was harvested in October and air dried at room temperature in dark place. The leaves, stems and roots of the plant were minced and extracted with n-hexane at 20°C: the extract was decanted and fresh n-hexane was added several times. The combined extracts were filtered through celite and concentrated under reduced pressure below 40°C in dim light.

2. Thin Layer Chromatography

T.L.C. was run using as adsorbent, silica gel G(manufactured by E. Merck). Plates(20cm ×20cm) were activated by heating at 120°C for 30min. Concentrated extract were spotted and developed in dim light, in ascending direction with the ether-n-hexane(1:4 v/v) mixture. Developed plates were visualized with iodine vapor and U.V. lamp. The separated band were removed from the plates and eluted from the silica gel with diethyl ether and concentrated in vacuo. TLC band of concentrated extract showed it was a mixture of at least 10 components, the rf values of which were 0.97, 0.85, 0.81, 0.72, 0.67, 0.52, 0.48, 0.35, 0.18 and Zero. The components of rf value of 0.85(A), 0.81(B) and 0.67(C) were separated as a yellow liquid(B) or as crystals (A and C: by crystallized from CCl₄-hexane mixture).

3. Equipment

Melting point were taken on a Kofler block, and were not corrected. Ultraviolet spectra were run on a Cary Model 2 UV-VIS spectrophotometer. The infrared spectra were determined on AgCl Cell with a Unicam SP 200 IR spectrophotometer. The proton N.M.R. spectra were recorded using a Varian EM 360 spectrometer system. Removal of solvents was carried out using Fisher Flash Evaporator under reduced pressure (water pump) at temperatures not exceeding 40°C in dim light. Since the polyacetylenic components are unstable, the compounds were stored in solution at 5°C in refrigerator.

III. Results and Discussion

The polyacetylenes from both the leaves and roots, although the quantities were different, proved to be identical. Three of them, occurring in high concentrations, were characterized by

Table 1. Spectral data of Polyacetylenes from *Chrysanthemum Sibiricum* F.

	Component (A): cis-ene-diyne m.p. 48–49°C	Component(B): trans-ene-diyne pale yellow oil	Component(C): m.p. 63°C
U. V. (n-Hexane)	$\lambda_{\text{max.}}$ nm	$\lambda_{\text{max.}}$ nm	$\lambda_{\text{max.}}$ nm
	318(ϵ 19,000)	321(ϵ 21,000)	347(ϵ 33,000)
	265(ϵ 4,500)	310(ϵ 21,000)	325(ϵ 40,000)
	250(ϵ 4,600)	269(ϵ 5,500)	306(ϵ 26,000)
	237(ϵ 7,400)	254(ϵ 4,100)	289(ϵ 14,000)
	227(ϵ 12,500)	238(ϵ 9,800)	269(ϵ 118,000)
	210(ϵ 6,200)	225(ϵ 14,200)	259(ϵ 58,000)
I. R. (neat, thin film)	cm^{-1}	cm^{-1}	cm^{-1}
	2240	2240	2210
	2140	2140	1740
	1640	1640	1630
	1585	1585	1230
	1350	1350	985
	1220	1280	
	1130	1095	
	945	1025	
	925	975	
730	900		
$^1\text{H-NMR}$ (CCl_4)***	δ (ppm)	δ (ppm)	δ (ppm)
	1.98(3) s	2.04(3) s	1.8 (2) tt J=6
	2.2 (4) m	2.1 (4) m	1.99(3) s
	4.0 (2) m	3.8 (2) m	2.05(3) s
	4.80(1) s(broad)	4.45(1) m	2.4 (2) dt J=6
	6.12(1) dd J=6+1.6	6.07(1) dd J=5.8+0.7	4.0 (2) t J=6
	6.60 (1) d J=5	6.20(1) d J=5.8	5.5 (1) d J=15
		5.9 (1) dt J=15+6	
		6.2 (1) dd J=15+10	
		6.7 (1) dd J=15+10	

*** All spectra were recorded at 60 MHz in CCl_4 soln.

Chemical shifts are reported in ppm relative to TMS(0).

melting points, UV, IR spectra and $^1\text{H-NMR}$ spectra (Table 1).

1. Components(A) and (B)

Component(A) shows a u.v. spectrum with maximum at 318nm without fine structure due to complicated end-groups in conjugation with the polyene chain. The same effect of the u.v. spectrum of (B) shows only weakly-defined

maxima at 321 and 310nm, while from the i.r. spectrum the presence of an enolether double bond could be recognised (730cm^{-1} : cis ethylenic hydrogen, 975cm^{-1} : trans ethylenic hydrogen, 1640cm^{-1} : conjugated double bond). The absorption bands at 2240 and 2140cm^{-1} indicate the presence of diyne group.

Assuming spiroketalenolether as plausible structures for these compounds based on the

above spectral data, the $^1\text{H-NMR}$ spectra(CCl_4 , internal TMS) can be assigned as follows:

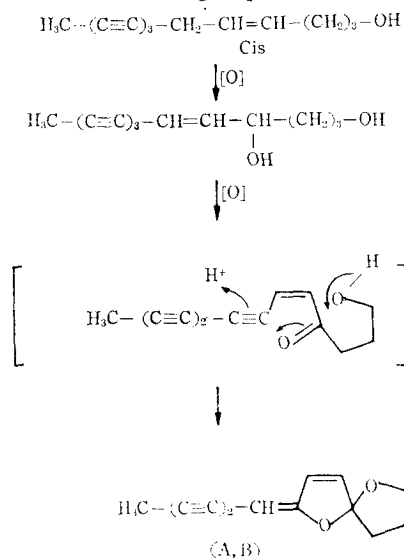
(A) 3 methyl protons attached to acetylene carbon(δ 1.98, singlet), 4 methylene protons(δ 2.2, multiplet), 2 methylene protons(δ 4.0, multiplet) adjacent to the oxygen, 3 cis-vinylic protons(δ 4.8, singlet (broad), δ 6.12 quartet $J=6.6$, δ 6.6 doublet $J=5$)

(B) 3 protons of methyl group attached to acetylene carbon(δ 2.04, singlet), 4 methylene protons(δ 2.1, multiplet), 2 protons of methylene adjacent to the oxygen(δ 3.8, multiplet), 3 trans-vinylic protons(δ 4.45, multiplet, δ 6.07, quartet, $J=6.5$, δ 6.2 doublet $J=5.8$)

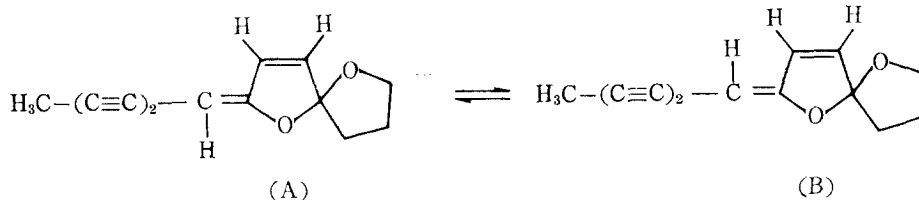
The trans-enoether proton always is shifted to higher field. The spectral data of these two constituents establish their structure as C_{13} Triyne-diene spiroketalenol ether(cis: A, trans: B).

It have been known that the feeding experiments with different labelled precursors established the biogenetic pathway to A and B as

shown in the following sequence¹²:



The two acetylenes can be isomerised by u. v. irradiation and also by acid treatment. The n. m. r. spectra, together with all these results, are in agreement with the structures A and B¹³:



2. Component(C)

The component(C) (m. p. 63°C , yellow crystal) shows the typical U. V. spectrum with fine structure of a triyne-diene chromophore. I. R. spectrum indicate the presence of unconjugated ester carbonyl group(1740 and 1230cm^{-1}), trans ethylenic hydrogen(985cm^{-1}), trans-trans configuration of the diene(1580 and 1630cm^{-1}) and acetylene(2225cm^{-1}).

This gave the same I. R. and U. V. spectrum, identical to that of a known¹⁴ triyne-diene acetate.

The proton NMR spectra as a triyne-diene acetate can be analysed as follows:

- δ 1.8(2) multiplet(t, t) $J=6$: methylene($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$)
- 1.99(3) singlet: methyl protons of acetyl group
- 2.05(3) singlet: methyl protons attached to acetylene carbon
- 3.4(2) multiplet(dt) $J=6$: methylene protons adjacent to vinyl group
- 4.0(2) triplet $J=6$: methylene protons $-\text{CH}_2-\text{O}-$

