

Acetylenic derivatives from some compositae plants[†]

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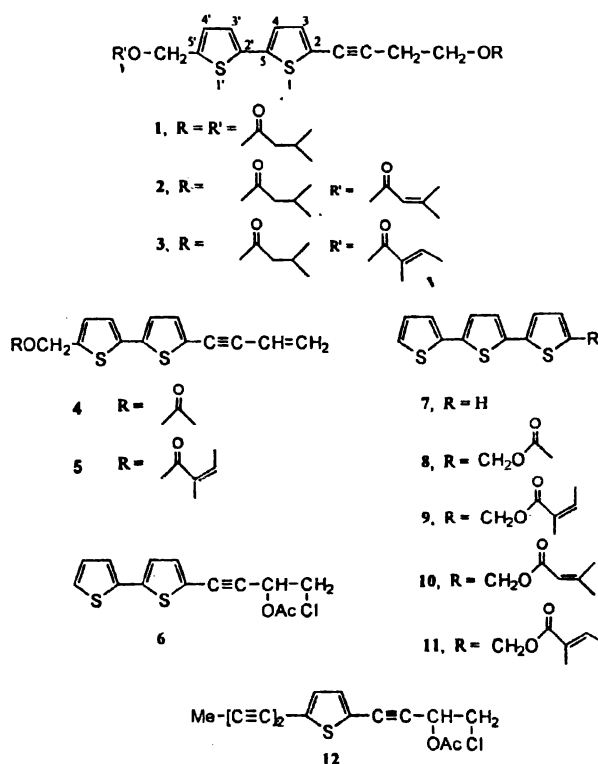
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The acetylenic derivatives isolated from six Compositae plants, viz. *Eclipta erecta* (roots), *Dicoma zeyheri* (roots), *Inula cuspidata* (aerial parts), *Cineraria fruticulorum* (whole plant), *Blainvillea acmella* (roots) and *Moscharia pinnatifida* (aerial parts) have been reviewed.

We have chemically examined half a dozen of Indian Compositae plants¹ which are rich in acetylenic compounds. Polyacetylenes are characteristic metabolites of Compositae and their biological properties also make them of interest to plant pathologists and pharmacologists. In this short review, we present the results of structure elucidation of three thiophene acetylenic esters from *Eclipta erecta*²⁻⁴, two furanoacetylenes from *Dicoma zeyheri*⁵ and a pair of pyranoacetylenic sulphoxides from *Inula cuspidata*⁶ in addition to some rare and interesting but known acetylenes from *Cineraria fruticulorum*⁷, *Blainvillea acmella*⁸ and *Moscharia pinnatifida*⁹.

Eclipta erecta Linn. (syn. = *E. alba* Hassh.; = *E. prostrata* L.) (tribe-Heliantheae) is a wild growing herb with white flowers. Previous work on this plant led to the isolation of a number of thiophene derivatives¹⁰. The co-occurrence of mono-, di- and trithiophene derivatives in this species is remarkable. During reinvestigation, the roots afforded three new dithiophene acetylenic esters which have been assigned structures as 5'-isovaleryloxymethylene-2-(4-isovaleryloxybut-3-ynyl)dithiophene 1, 5'-seneciolyloxymethylene-2-(4-isovaleryloxybut-3-ynyl)dithiophene 2 and 5'-tigloyloxymethylene-2-(4-isovaleryloxybut-3-ynyl)-dithiophene 3 along with 2-acetoxymethylene-5'-(but-3-en-1-ynyl)dithiophene 4, 2-angeloyloxymethylene-5'-(but-3-en-1-ynyl)dithiophene 5, 2-(3-acetoxy-4-chlorobut-1-ynyl)-dithiophene 6, terthienyl 7 and the corresponding acetoxo 8, angeloyloxy 9, seneciolyoxy 10, tigloyloxy 11 methylene derivatives and 2-(3-acetoxy-4-chlorobut-1-ynyl)-5-(pent-1,3-diyynyl)thiophene 12.

The structures of dithiophene acetylenic esters 1-3 were established by detailed spectral studies. Their ultraviolet spectra displayed broad absorption maxima at 335 nm characteristic of dithienyl chromophoric system and were comparable with the literature^{11,12}. The presence of acetylenic linkage and ester function was ascertained by observing sharp IR bands at 2240 and 1740 cm⁻¹ respectively. The molecular formula C₂₃H₂₈S₂O₄ for 1 was

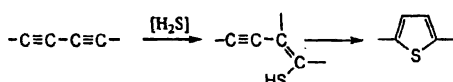


arrived from accurate mass measurements of molecular ion peak at *m/z* 432.142. Its ¹H nmr spectrum showed the presence of two distinct isovalerate residues. Two upfield methyl doublets at δ 0.91 and 0.95 with coupling constants 7 Hz, a pair of methylene doublets at δ 2.22 and 2.23 (*J* 7 Hz each) and a multiplet centred at δ 2.12 for methine protons indicated the presence of isovalerate functions which was further confirmed by the appearance of characteristic peaks at *m/z* 330 [M-C₄H₉COOH]⁺ and 85 [C₄H₉CO]⁺ in the mass spectrum. A set of triplets at δ 2.79 and 4.25 corresponded to adjacent ≡C-CH₂ and CH₂-O protons. A singlet at δ 5.21 was assigned to -CH₂-O group on the other side of thiophene ring. Signals in the aromatic region at δ 7.02 (d), 7.00 (d), 6.97 (d) and 6.96 (d) each with coupling constant 3.5 Hz were assignable to H-3', H-3, H-4' and H-4 pro-

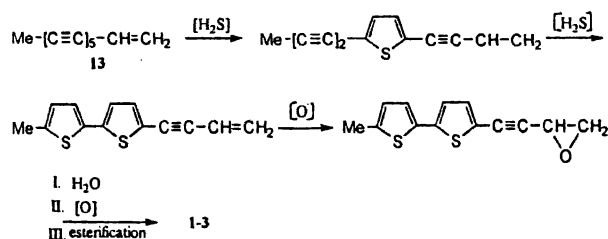
[†]Dedicated to Professor D. Nasipuri on the occasion of his 75th. birth anniversary.

tons. The sequence of protons was established by spin decoupling experiments. The ^1H nmr spectra of compounds **2** and **3** were very much similar to that of **1** barring the signals of ester functions. Pair of methyl doublets was replaced by a only doublet at δ 0.93 implying the presence of one isovalerate residue and appearance of additional signals for seneciyoxy (δ 2.19, 1.89, 5.79) and tigloyloxy (δ 1.83, 1.80, 6.87) esters in **2** and **3** respectively, confirmed their structures. The relative position of ester moieties could be deduced by comparing chemical shifts of methylene groups attached to these functions with those of the corresponding diacetate isolated from *Porophyllum*¹².

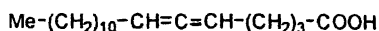
Biogenetically these dithiophenes are probably derived from acetylenic precursors as these still have acetylenic bonds. The key step is the addition of H_2S or its biochemical equivalent to conjugated diyne system to form a thiophene ring. Addition of two equivalent of H_2S to widespread



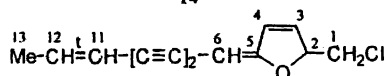
tridecapentayne **13** results in the formation of dithienyl system which on subsequent hydrolysis, oxidation and esterification gives esters **1-3**. Feeding experiments have established this assumption earlier for several other dithiophenes¹³.



Dicoma zeyheri Sond. (tribe-Mutisieae) is an annual herb. Chemical examination of its roots afforded β -farnesene, α -humulene, 9β -hydroxydehydrozalanin C, isocomene, β -isocomene, laballenin acid **14** and an inseparable mixture of furanoacetylenes **15** and **16** named as *5E*- and *5Z*-zeyherin.



14



15, 5E

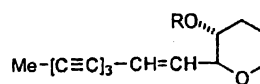
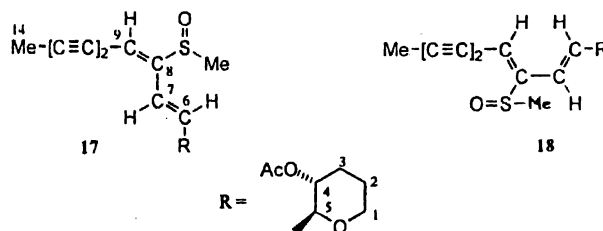
16, 5Z

The spectral studies of the mixture indicated that these isomers differed only in the stereochemistry of the 5,6-double

bond. As two isomers were present in unequal amount therefore the assignment of their signals became easier. Methylene protons (H-1 and H-1') displayed signals at δ 3.59, 3.60 and 3.66, 3.76 as double doublets with large geminal coupling while methine proton (H-2) gave four-fold doublets at δ 5.42 and 5.48. Furanic H-3 and H-4 protons appeared as double doublets at δ 6.53 and 6.76 and olefinic H-6 proton gave broad singlets at δ 5.02 and 4.69. *Z*-Isomer showed a more downfield shifted H-6 signal (δ 5.02) in comparison to *E*-isomer. A broad doublet at δ 5.60 and a doublet quartet at δ 6.30 were assigned to H-11 and H-12 olefinic protons with *trans* geometry. Methyl protons (H-13) appeared as double doublets at δ 1.81 and 1.82 corresponding to different isomers. The molecular formula $\text{C}_{13}\text{H}_{11}\text{OCl}$ was deduced from high resolution mass spectrometry.

These acetylenes are biogenetically formed from acetylenic epoxides. Epoxides are present as co-metabolites and the halides are formed by nucleophilic opening of the epoxide ring with HCl to give chlorohydrins. Subsequent cyclization of chlorohydrins gave cyclic ether containing chlorine, **15** and **16**.

Inula cuspidata C.B. Clarke (tribe-Inuleae) is an annual herb and collected from surroundings of North-Delhi. Chemical investigation of its aerial parts gave β -farnesene, geranyl linalool, a pair of inseparable pyranoacetylenes containing sulphoxide functions **17** and **18** in addition to ichthyothanol and its acetate¹⁴ **19** and **20**.



19, R = H

20, R = Ac

The molecular formula of isomeric sulphoxides was arrived as $\text{C}_{17}\text{H}_{20}\text{O}_4\text{S}$ from high resolution mass spectrometry. The acetylenic nature of the compounds was established by their characteristic UV and IR spectra (2220 cm^{-1}). The ^1H nmr spectra were recorded in CDCl_3 as well as C_6D_6 and their detailed assignments are depicted in Table 1.

Spin decoupling allowed the assignment of all signals

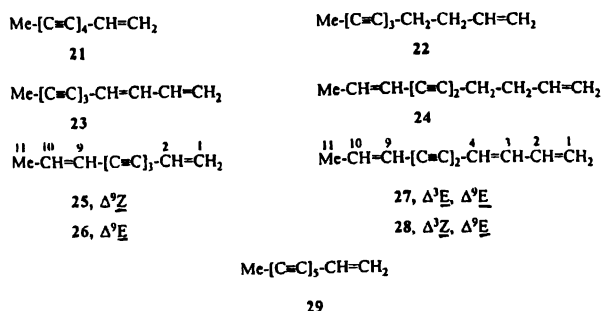
Table 1. ¹H NMR Data of compounds 17* and 18*

	17		18	
	CDCl ₃	C ₆ D ₆	CDCl ₃	C ₆ D ₆
H-1	3.99 dbr	3.61 m	3.99 dbr	3.61 m
H-1'	3.42 ddd	2.92 ddd	3.42 ddd	2.92 ddd
H-4	4.63 d	4.68 dd	4.58 m	4.68 m
H-5	3.79 ddd	3.50 m	3.79 ddd	3.50 m
H-6	5.92 dd	6.07 dd	5.92 dd	5.97 dd
H-7	6.77 d	7.05 d	6.81 d	7.09 d
H-9	6.34 sbr	6.71 sbr	6.32 sbr	6.72 sbr
H-14	2.05 d	1.36 d	2.04 d	1.35 d
SOMe	2.64 s	2.18 s	2.66 s	2.12 s
OAc	2.01 s	1.67 s	2.05 s	1.74 s

*H-2 2.05 m, H-2', 1.74 m, H-3 2.17 m, H-3' 1.06 m (CDCl₃); *J* (Hz) : 1,1' = 1', 2 = 13; 1'2' = 4; 3,4 = 4.5; 3',4 = 3.5 = 10; 5,6 = 6.5; 6,7 = 15; 9,14 = 1.3.

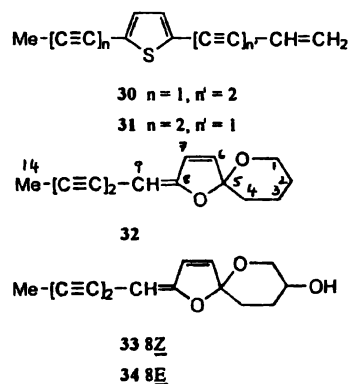
which were in part very similar to those of ichthyothanol acetate 20. The position of the sulphoxide group was established from the chemical shifts of H-7 and from the coupling of the olefinic proton with the acetylenic methyl group. The observed magnitude is characteristic for this situation. Surprising, there were the small chemical shift differences of H-9 in the two isomers. Normally in such sulphoxides the *cis*-olefinic proton is more deshielded¹⁵. Perhaps due to steric hindrance the 7,8-bond was in a *S-cis*-conformation, where the H-9 proton would be deshielded by the 6,7-double bond (vide expanded structure). The assignment of the configurations of the two isomers caused difficulties. However, the stronger Eu(fod)₃ induced shift of the acetate signal would support the proposed stereochemistry, if the assumed configurations were valid.

The aerial parts and roots of *Cineraria fruticulorum*⁷ Hutch. (tribe-Senecioneae) on chemical examination gave linear acetylenes 21-28 containing C₁₁ and tridecapentayne 29, a C₁₃ acetylene. Acetylenes containing C₁₁ are characteristic of this genus.



The roots of *Blainvillea acmella*⁸ Linn. (tribe-

Heliantheae) afforded a pair of isomeric monothiophenes 30 and 31 while aerial parts of *Moscharia pinnatifida* Ruiz. et. Pav. (tribe-Mutisieae) gave spiroketals 32-34 on chemical investigation⁹. The identity of known acetylenes was established by direct comparison or by comparing their spectral data from literature.



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