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NEMATICIDAL POLYACETYLENES, 3Z,11E- AND 3E,11E-TRIDECA-1,3,11-TRIENE-5,7,9-TRIYNE FROM CARTHAMUS TINCTORIUS L

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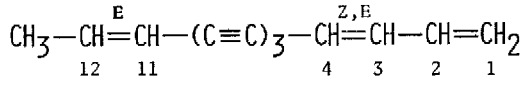
In the course of studies of nematicidal substances in higher plants, two nematicidal polyacetylenes[1] were discovered in Carthamus tinctorius L

We now report the isolation and structural elucidation of these polyacetylenes, I and II The nematicidal fraction containing I and II (83 17) was easily obtained by column chromatography (silica gel, elution with n-hexane or n-pentane) of benzene extracts of C tinctorius Difficulty of the clear separation of these components from each other is based on the photoisomerisation, by which I and II give same equilibrium mixture (I II, 37 63) Thus, the fraction was subjected to a preparative high speed LC (BONDAPAK C_{18}/CORASIL, 4 6 mmID x 100 cm, 3 ml/min, 30 % H_2O in MeOH) under the dark condition and separated into the component I and II (Retention time, 22 and 32 min) The component I, oil, $C_{13}H_{10}$(M^+,166) has ν_{max}(CCl_4), 2215, 2180, 996, 916 and 664 cm^{-1} and λ_{max}(Et_2O), 382, 366, 354, 342, 331, 319, 310, 299, 289, 274, 243, 234 and 224 nm (ε 3000,18300, 8300, 24700, 10900, 17800, 10000, 12500, 52100, 53500, 27700, 30000, 32800) The uv spectrum is characteristic of the conjugated ene-triyne-diene group[2),3)] The nmr spectrum of I in CCl_4 shows the presence of a vinyl methyl (1 88, 3H, dd J=7, 2) and seven olefinic protons (6 88, 1H, octet J=16 5, 11, 10, 6 53, 1H, t J=11, 6 38, 1H, dq J=16, 7, 5 2-5 8, 4H, m) The E-configuration of the methyl vinyl group was established by decoupling technique Irradiation at 1 88 caused the C_{12}-H (6 38, dq) and C_{11}-H signal to collapse to a AB type doublets (6 38 and 5 53, J=16) Terminal diene of I must have 3Z-configuration because the signals at 6 53 (t J=11) and 6 88 (octet J=16 5, 11, 10) are assigned to C_3-H and C_2-H, respectively From the above data, the component I was concluded to be 3Z,11E-trideca-1,3,11-triene-5,7,9-triyne.

The component II, oil, $C_{13}H_{10}$(M^+,166) has ν_{max}(CCl_4), 2335,2200, 998, 946, 916 and 665 cm^{-1}



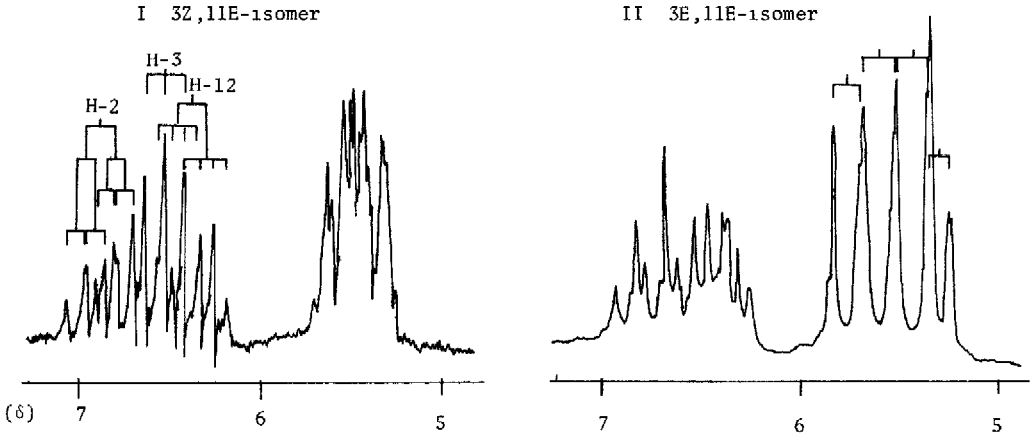


Figure 1 Olefinic regions of nmr spectra of I and II

The uv spectrum of II was almost identical with that of I The nmr spectrum of II (CCl_4-acetone-d_6) shows a vinyl methyl (1 87, 3H, dd J=8, 1 5) and two groups of olefinic protons (5 2-5 9, 4H, 6 2-7 0, 3H, m) The olefinic protons of higher field consisted of four doublets (5 74, 1H, d J=15, 5 49, 1H, d J=16, 5 41, 1H, d J=16, 5 27, 1H, d J=10), which are assignable to C_1, C_4 or C_{11} protons The component II was determined to be 3E,11E-isomer of I because only one of the above doublets has small coupling constant for Z-configuration

Sórensen[2] and Bohlmann[3] have reported the isolation of trideca-1,3,11-triene-5,7,9-triyne without detailed description about C_3-configuration

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Footnote and references

1) Nematicidal activities of I and II to Aphelencoides besseyi were observed after 24 hours I, 10 ppm, 30 % II, 2 ppm, 85 % mortality The biological study will be reported in detail elsewhere

2) J S Sorensen and N A Sorensen, Acta Chem Scand , 12, 756 (1958)

3) F Bohlmann and P Herbst, Chem Ber , 91, 1631 (1958), F Bohlmann, S Kohn and C Arndt, Chem Ber , 99, 3433 (1966)