

Nuclear Magnetic Resonance Spectrum of Phytoene

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Phytoene, a colorless polyene, occurs widely in nature¹⁾ and is thought to play an important role in the biosynthesis of carotenoids.^{2,3)} Its structure is considered to be 2, 6, 10, 14, 19, 23, 27, 31-octamethyldotriacontanonaene - 2, 6, 10, 14, 16, 18, 22, 26, 30, mainly on the basis of its chemical properties.⁴⁾ The NMR spectrum has been reported by Davis *et al.*⁵⁾ and by Jungalwala *et al.*⁶⁾ However, only the values for the methyl groups were reported in the former paper,⁵⁾ whereas the chart

shown in the latter paper has peaks in the region of τ 8.5—9.3 which are unexplainable on the basis of the structure reported⁴⁾; besides, the relative intensities of the respective peaks are not given. The NMR spectrum has, accordingly, been re-measured on a pure sample of phytoene in order to check the validity of the published spectrum and the structure.

The method of the extraction and purification of phytoene from tomatoes was practically the same as that previously reported,⁶⁾ but two additional preparative thin-layer chromatographic separations (plate: 20 cm \times 20 cm, silica gel G activated for 2 hr at 110°C, thickness: 1.0 mm, solvent: hexane-ether, 99-1) were carried out. The position of phytoene was determined by spraying the plate with a 0.5% solution of potassium permanganate after covering it with a slitted cardboard (slits: 0.3 mm with 3-cm intervals). The position of the plate was marked, and the

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silica gel on that portion was scraped off and eluted with freshly-distilled ether-hexane (50 : 50). Phytoene, obtained by the removal of the solvent *in vacuo*, was used for the measurement.

The NMR spectrum of phytoene was run in deuteriochloroform (concentration 10 mg/0.5 ml), with tetramethylsilane as internal reference, using a

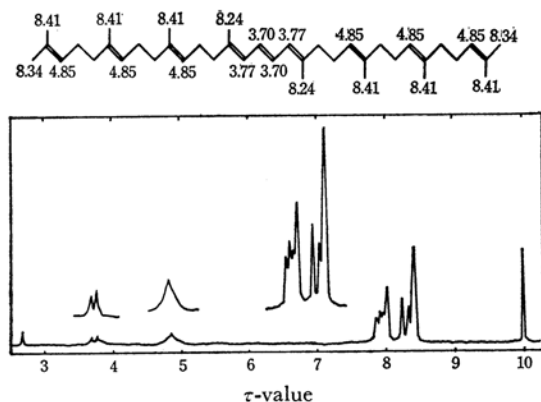


Fig. 1. NMR spectrum and its assignment of phytoene in CDCl_3 at 60 Mc/sec.

JEOL 60 Mc 3H-60 spectrometer. In the following the observed τ values (see Fig. 1) are recorded, together with the relative numbers of protons observed (obtained by electronic integration) and the relative numbers of protons expected (shown in parentheses): 3.70, central $-\text{CH}=$ 1.9 (2); 3.77, $-\text{CH}=$ adjacent to central unsaturation 1.9 (2); 4.85, other $-\text{CH}=$ 5.7 (6); 7.85–8.02 $-\text{CH}_2-$ 24.2 (24); 8.24, central $-\text{CH}_3$ 6.0 (6); 8.34, terminal $-\text{CH}_3$ (cis to H) 6.0 (6); 8.41 other $-\text{CH}_3$ (trans to H) 18.3 (18). These assignments are based on the spectra of the polyisoprenoid chains in naphthoquinone⁷ and carotenoids,^{5,8} and also on a cyclic triene.⁹ In the present experiment, the fine structure of the $-\text{CH}=$ protons was not well resolved, possibly because of the large size of the phytoene molecule. However, the NMR spectrum is in good agreement with the structure of phytoene.

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