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Structural Characterization of Ficaprenol-11 by ^{13}C Nuclear Magnetic Resonance

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The location of the internal *trans* and *cis* isoprene units in ficaprenol-11 isolated from *Ficus elastica* was determined by ^{13}C nuclear magnetic resonance. The alignment of the isoprene units was estimated to be in the order: ω-terminal unit, three *trans* units, six *cis* units and α-terminal *cis* alcohol unit.

The widespread occurrence of polyisoprenoid alcohols from C_{45} to C_{100} in chain length has been recognized in leaves of higher plants and in many mammalian tissues. Most of the polyprenols isolated from higher plants have consisted of *cis* and *trans* isoprene units, except for solanesol, which is recognized to be composed of all-*trans* isoprene units. A ^{1}H n.m.r. study of ficaprenols isolated from *Ficus elastica* suggested that ficaprenol-10 (C_{50}), -11 (C_{55}) and -12 (C_{60}) contained three internal *trans* units and five, six and seven internal *cis* units respectively (Stone *et al.*, 1967). A similar composition of internal isoprene units was also reported for castaprenol-11, -12 and -13 (Wellburn & Hemming, 1966), betulaprenol-10, -11 and -12 (Wellburn & Hemming, 1966) and cleomeprenol-9, -10 and -11 (Suga *et al.*, 1975). The expected alignment of *trans* and *cis* units in these polyprenols was in the order: ω-terminal unit, three *trans* units, several *cis* units and α-terminal *cis* alcohol unit, which was estimated on the basis of the

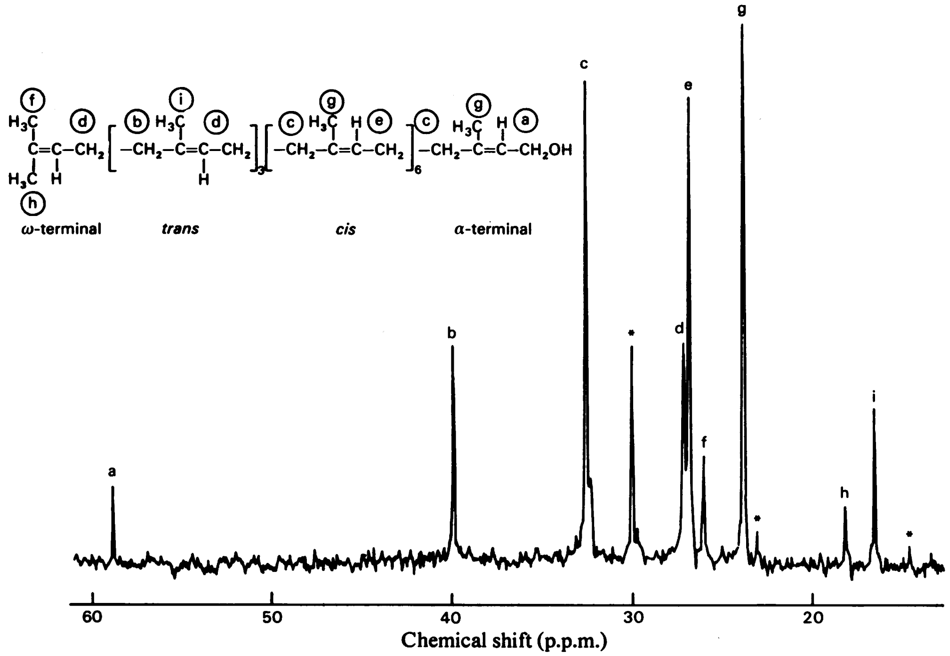


Fig. 1. *^{13}C n.m.r. spectrum of ficaprenol-*11 (*aliphatic part*)

Letters above the peaks of the spectrum correspond to the carbon atoms as indicated in the structure of ficaprenol-11 shown. The asterisks indicate peaks due to an impurity. The reference compound was tetramethylsilane.

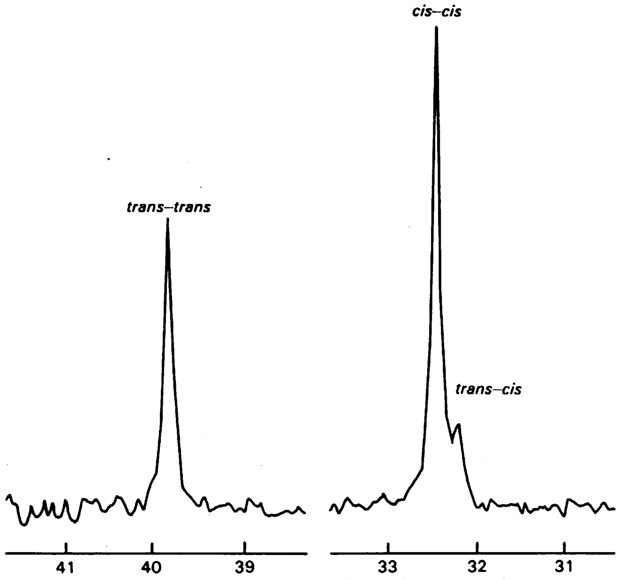


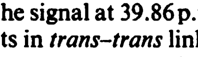
Fig. 2. *Signals due to $C_{(1)}$ methylene carbon atoms in trans and cis units, which correspond to signals b and c in Fig.* 1
The reference compound was tetramethylsilane.

mechanism of the formation of polyprenols. However, there is no direct evidence to prove the location of the internal *trans* and *cis* units as yet.

In previous work, we found new signals attributed to *cis–cis-*, *cis–trans-* and *trans–trans-*linkages in the ^{13}C n.m.r. spectrum of *cis–trans-*isomerized polyisoprenes (Tanaka & Sato, 1976). This method was applied to the determination of the location of the internal *trans* and *cis* units in ficaprenol-11.

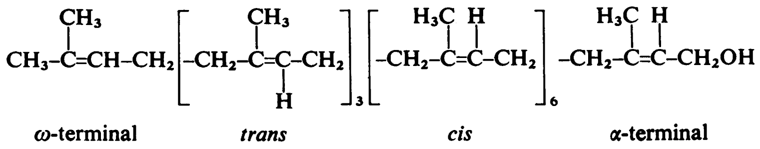
Ficaprenols were isolated from lipids extracted from the leaves of *F. elastica* by the method of Stone *et al.* (1967). Ficaprenol-11 was purified by means of gel-permeation chromatography by using a column packed with a polystyrene gel having a molecular-weight-exclusion limit of 3000. The molecular weight of ficaprenol-11 was confirmed from its elution volume calibrated with synthetic isoprene oligomers. The ^{13}C n.m.r. spectrum was obtained by using a JEOL FX-100 spectrometer. Measurements were made at room temperature (approx. 23°C) in [^{2}H]chloroform.

The ^{1}H n.m.r. spectrum of ficaprenol-11 coincided with that reported by Stone *et al.* (1967). The intensity ratio of the *cis-* to *trans-*methyl-proton signals indicated the presence of three internal *trans* units and six internal *cis* units. The ^{13}C n.m.r. spectrum of ficaprenol-11 was assigned by comparing their chemical shifts with those of the *cis–trans-*isomerized polyisoprenes squalene and geraniol. The assignment of the aliphatic carbon atoms was as indicated in Fig. 1. As shown in Fig. 2, the signal due to the $C_{(1)}$ methylene carbon atom in *cis* isoprene units split into two peaks at 32.37 and 32.17 p.p.m., where the carbon atoms are designated as follows:



$$-C_{(1)}-\overset{\overset{\displaystyle C_{(5)}}{|}}{C_{(2)}}=C_{(3)}-C_{(4)}-$$

These peaks were assigned to the $C_{(1)}$ carbon atoms in *cis* units being linked to *cis* and *trans* units in order of increasing magnetic field on the basis of the assignment for *cis–trans-*isomerized polyisoprenes (Tanaka & Sato, 1976). On the other hand, no splitting was observed for the $C_{(1)}$ methylene carbon atom signal of *trans* units; the signal at 39.86 p.p.m. corresponded to the *trans* units in *trans–trans* linkage. The intensity ratio of the *trans–trans*, *trans–cis* and *cis–cis* signals was 2.8 : 0.9 : 6.3. It seems reasonable to assume that the $C_{(1)}$ methylene carbon atom in the α-terminal *cis* unit resonated at 32.37 p.p.m., overlapping with the *cis–cis* signal, and the $C_{(1)}$ methylene carbon atom in the *trans* unit adjacent to ω-terminal unit showed the same chemical shift as in the *trans–trans* linkage, which was confirmed in the spectrum of squalene. On the basis of these facts, the sequence structure of ficaprenol-11 was clearly determined as follows:



$$CH_3\text{-}\overset{CH_3}{C}{=}CH\text{-}CH_2\left[\text{-}CH_2\text{-}\overset{CH_3}{C}{=}\underset{H}{C}\text{-}CH_2\right]_3\left[\text{-}CH_2\text{-}\overset{H_3C}{C}{=}\overset{H}{C}\text{-}CH_2\right]_6\text{-}CH_2\text{-}\overset{H_3C}{C}{=}\overset{H}{C}\text{-}CH_2OH$$

This alignment of the isoprene units proves the validity of the mechanism for biosynthesis of *cis–trans* polyprenols.

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