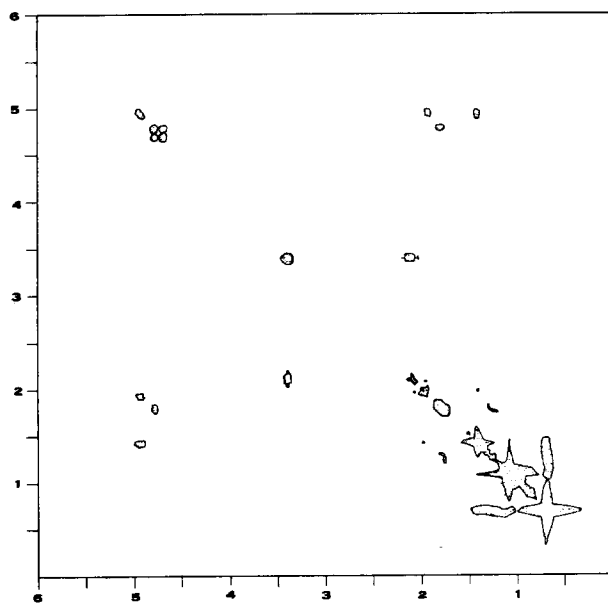




methylene was coupled with the allylic methine C-13 and with the vinylic proton C-11. This latter was correlated with the vinylic C-10' and the allylic methylene C-9. The OH-bearing C-13' methylene was coupled with the C-13 methine and finally protons at C-14' were coupled with each other and correlated with the allylic methylene C-15. Homonuclear decoupling experiments, when significant, confirmed these correlations.



As for geometry of the trisubstituted double bond, it was assigned the *E* configuration on the basis of the shieldings of the vinylic methyl group in the  $^1\text{H}$ - ( $\delta$  1.33) (5) and  $^{13}\text{C}$ -nmr ( $\delta$  16.05) spectra (3).

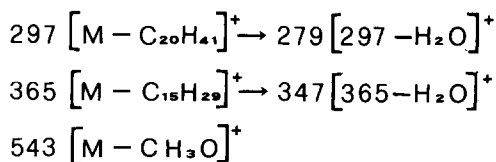
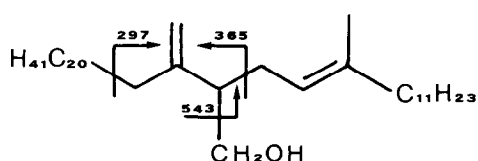
Table.  $^{13}\text{C}$ -nmr data of 1

1	22.71 $\text{CH}_3^a$	11	121.95 CH	21	37.42 $\text{CH}_2^c$	31	22.62 $\text{CH}_3^a$
2	27.96 CH	12	29.09 $\text{CH}_2$	22	32.74 $\text{CH}^d$	2'	22.71 $\text{CH}_3^a$
3	39.35 $\text{CH}_2^b$	13	40.66 CH	23	36.89 $\text{CH}_2^c$	6'	19.73 $\text{CH}_3$
4	24.43 $\text{CH}_2^c$	14	136.75 C	24	24.79 $\text{CH}_2^b$	10'	16.05 $\text{CH}_3$
5	37.23 $\text{CH}_2^c$	15	34.81 $\text{CH}_2^e$	25	37.42 $\text{CH}_2^c$	13'	64.06 $\text{CH}_2$
6	32.79 $\text{CH}^d$	16	25.25 $\text{CH}_2^e$	26	32.69 $\text{CH}^d$	14'	110.52 $\text{CH}_2$
7	37.42 $\text{CH}_2^c$	17	37.42 $\text{CH}_2^c$	27	37.23 $\text{CH}_2^c$	18'	19.73 $\text{CH}_3$
8	25.36 $\text{CH}_2^e$	18	32.79 $\text{CH}^d$	28	24.48 $\text{CH}_2^b$	22'	19.73 $\text{CH}_3$
9	40.05 $\text{CH}_2$	19	36.64 $\text{CH}_2^c$	29	39.35 $\text{CH}_2$	26'	19.73 $\text{CH}_3$
10	150.04 C	20	24.79 $\text{CH}_2^b$	30	27.96 CH	30'	22.62 $\text{CH}_3^a$

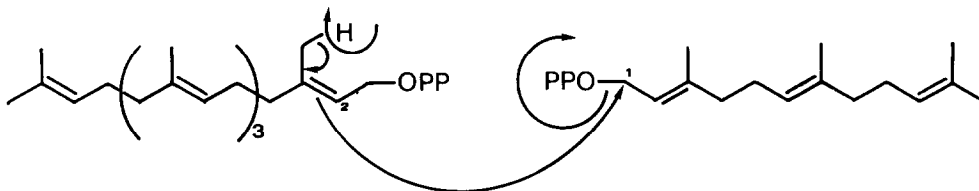
a,b,c,d,e Assignments bearing the same superscript may be reversed

In spite of the molecular formula, the  $^{13}\text{C}$ -nmr spectrum of 1 showed only 24 signals: DEPT experiments (7) allowed us to identify the carbon types while quantitative measurements, obtained by inverse-gated decoupling (8), gave us the intensity values of these signals. Assignment of the individual chemical shift values presented in the Table was based on earlier assigned spectra of analogous isoprenoids (9).

The presence of eight methyls and seven aliphatic methylenes suggested that 1 was a linear isoprenoid with an hydroxymethyl group. The fragmentation pattern in the electron impact mass spectrum with peaks at  $m/z$  543, 365, 347, 297 and 279 was essential in attributing the position of the functional residue unambiguously in the chain.



Tetraterpenes represent a rather small class of isoprenoids: from a biogenetic point of view carotenoids are formed from two GGPP units through a tail-to-tail dimerization; other examples of tetraterpenes are the  $C_{40}$  polyprenols (10) formed from FPP by adding in a head-to-tail fashion other  $C_5$  units and the recently reported (11)  $C_{40}$  diols with a chain composed of two  $C_{20}$  units joined head-to-head. In this context 1 represents a new type of tetraterpene presumably formed from geranylarnesyl and farnesyl pyrophosphates with a mechanism as reported below which allows a linkage between the C-2 of the  $C_{25}$  unit and the C-1 of the  $C_{15}$  one.



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## REFERENCES AND NOTES

1. The mass spectrum was obtained at 12 eV on a Kratos MS 30 mass spectrometer with a source of 150°C.
2. IR:  $\nu_{\max}^{\text{CCl}_4}$  1740, 1660, 1240  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr:  $\delta$  0.81 (d, 9H), 0.83 (d, 3H), 0.84 (d, 12H), 1.57 (s, 3H), 2.03 (s, 3H), 4.04 (d, 2H), 4.76 and 4.65 (ss, 2H), 5.07 (t, 1H).
3.  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr spectra were performed on a Bruker WM 500 FT and a Varian XL 200 spectrometers in  $\text{CDCl}_3$  solns using TMS as internal standard.
4. This experiment was run with a microprogram identical with that one described in the Varian XL 200 software manual (using 256x1024 data point matrix, transforming 1024 data points in both domains, spectral width 1200 Hz in both domains).
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8. This experiment was run with a microprogram identical with that one described in the Varian XL 200 software manual (pulse interval 12 sec, pulse width 5  $\mu\text{sec}$ ).
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