## A BIOGENETICALLY NEW TETRATERPENE ALCOHOL FROM ELODEA CANADENSIS

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Summary. On the basis of spectroscopic data structure 1 is proposed for a tetraterpene alcohol isolated from *Elodea canadensis*. A new biogenetic route is suggested for its formation.

In this paper we wish to report the characterization of a biogenetically now tetraterpone alcohol isolated from the ethereal extract of the aquatic plant *Elodea canadensis* L.C.H. Richard, which was attributed structure 1 on the basis of its spectral evidences.

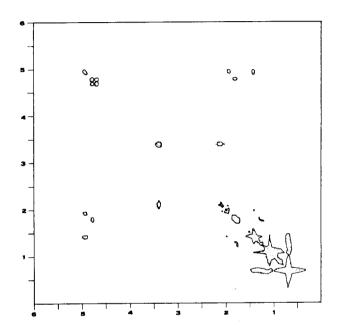
It was an oil,  $\left[\alpha\right]_0$  -31° (CHCl<sub>3</sub>), which showed in the electron impact mass spectrum (1) a molecular ion at m/z 574 corresponding to  ${}^{\rm C}_{40}{}^{\rm H}_{70}{}^{\rm O}$  and in the IR spectrum significant absorptions at 3840, 3880, 1880 and 1885 cm<sup>-1</sup> attributable to a hydroxyl group and to isolated double bonds. Acetylation with acetic anhydride under mild conditions in dry pyridine gave the corresponding acetate (2),  $\left[\alpha\right]_0$  -20° (CHCl<sub>2</sub>).

Functional groups of 1 were confirmed by nmr.  $^{1}$ H-nmr (500 HHz) (3): vinylic protons at  $\delta$  5.09 (t, 1H, J = 6.9 Hz), 4.94 and 4.84 (ss, 2H) and OH-bearing methylene at  $\delta$  3.55 (m, 1H);  $^{13}$ C-nmr (50.28 HHz) (3): olefinic carbons at  $\delta$  150.04, 136.75, 121.95, 110.32 and hydroxymethyl carbon at  $\delta$  34.09.

Desides those already reported, the  $^{1}$ H-nmr spectrum presented signals attributable to eight methyl doublets appearing as three groups in a 3 : 1 : 4 ratio centered at 6 0.31 (J = 0.3 Hz), 0.03 (J = 6.3 Hz) and 0.34 (J = 6.3 Hz) respectively, a vinylic methyl at 6 1.59 and seven allylic protons as three systems in a 1 : 2 : 4 ratio resonant at 6 2.26, 2.12 and 1.96.

Two-dimensional proton homonuclear chemical shift correlation spectrum (Figure 1) (4) allowed us to obtain unambigues data on the structure of the functional residue of 1: the C-12

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 2 configuration on the basis of the shieldings of the vinylic methyl group in the  $^{1}\text{H-}$  (§ 1.39) (5) and  $^{13}\text{C-nmr}$  (§ 16.05) spectra (3).

				Ta	able.	13 C-nmr	data of	1			
1	22.71	CH <sub>3</sub> a	11	121.95	СН	21	37.42	CH <sub>2</sub> c	31	22.62	сн <sub>з</sub> а
2	27.96	CH	12	29,09	CH <sub>2</sub>	22	32.74	CII	2'	22.71	CH <sub>3</sub> a
3	39.35	CH <sub>2</sub>	13	48.66	CH	23	36.39	CH <sub>2</sub> <sup>c</sup>	6'	19.73	CH <sub>3</sub>
4	24.43	CH <sub>2</sub> b	14	136.75	C	24	24.79	CH <sub>2</sub> b	10'	13.05	СНЗ
5	37.23	CH <sub>2</sub> c	15	34.81	CH <sub>2</sub>	25	37.42	CH <sub>2</sub> <sup>c</sup>	13'	64.06	CH <sub>2</sub>
6	32.79	CIId	16	25.25	CH₂ <sup>e</sup>	26	32.69	CH	14'	110.32	CII <sub>2</sub>
7	37.42	CH <sub>2</sub> C	17	37.42	CH <sub>2</sub> c	27	37.23	CH <sub>2</sub> <sup>c</sup>	18'	19.73	CII3
3	25.33	CH <sub>2</sub> e	13	32.79	CH	28	24.48	CH <sub>2</sub> <sup>b</sup>	22'	19.73	CH <sub>3</sub>
Э	40.05	CH <sub>2</sub>	19	36.64	CH <sub>2</sub> .	29	39.35	CH <sub>2</sub>	26'	19.73	СНЗ
10	150.04	C	20	24.79	CII <sub>2</sub>	30	27.96	CII	30'	22.32	CH <sub>3</sub>

 $\hbox{a,b,c,d,e}_{\hbox{\sc Assignments bearing the same superscript may be reversed}$ 

In spite of the molecular formula, the <sup>13</sup>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 sarlier assigned spectra of analogous isoprenoids (8).

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 fractional residue unambiguously in the chain.

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

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## REFERENCES AND NOTES

- 1. The mass spectrum was obtained at 12 eV on a Kratos  ${
  m MS}$  30 mass spectrometer with a source of 150°C.
- 2. IR:  $v_{\text{max}}^{\text{CCl}_4}$  1740, 1660, 1240 cm<sup>-1</sup>; <sup>1</sup>H-nmr: § 0.81 (d, 9H), 0.83 (d, 3H), 0.84 (d, 12H), 1.57 (s, 3H), 2.03 (s, 3H), 4.04 (d, 2H), 4.78 and 4.85 (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 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 µsec).
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