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# TERPENOIDS CXIV: LYRATOL, A NEW $C_{10}$ ALCOHOL FROM CYATHOCLINE LYRATA[1]

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In the course of an investigation[2] of the essential oil from Cyathocline Lyrata, a new alcohol has been isolated for which we propose the name lyratol and the structure I. This alcohol analyzes for the molecular formula $C_{10}H_{16}O$ (mass spectral mol. wt., 152) and possesses the following physical properties: b.p. 105° (bath)/2 mm, $n_D^{30}$ 1.4761, $\alpha_D$ + 62.3 (C, 4.6 in $CHCl_3$). It showed no absorption maximum in the UV spectrum. Its IR spectrum indicated the presence of OH and C=C (in particular, $C{=}CH_2$, 888 $cm^{-1}$).

The N.M.R. spectrum[3] of lyratol (shown in part in Figs. 1 and 2) provided enough information for deducing the complete structure of this alcohol. Two methyl groups of the type $CH_3 - C{=}CH$ were indicated by peaks at $\tau$ 8.40 and 8.31 displaying long-range coupling. A one-proton singlet at $\tau$ 7.22 which disappeared on shaking the sample with $D_2O$ corresponded obviously to a hydroxy proton. The area under the peaks between $\tau$ 3.8-5.3 represented six olefinic protons. A multiplet centered at $\tau$ 6.38 corresponded to one proton and a singlet at $\tau$ 6.09, to two protons.

Goodlett[4] has described the use of trichloroacetyl isocyanate (TAI) for distinguishing between different types of alcohols. Addition of TAI to a solution of lyratol in $C_6D_6$ replaced the $-O-\underline{H}$ singlet at $\tau$ 7.72 with a $-O-CO-N\underline{H}-COCCl_3$ peak at $\tau$ 1.44 and displaced the two-proton peak at $\tau$ 6.09 to $\tau$ 5.56. This downfield displacement of 0.53 ppm is characteristic of a primary alcohol.[4] The singlet nature of this methylene signal demonstrated that lyratol contains a primary alcohol function without any protons on the adjacent carbon ($HO-CH_2-\overset{|}{\underset{|}{C}}-$). We have found[5] that the β-olefinic protons of allylic

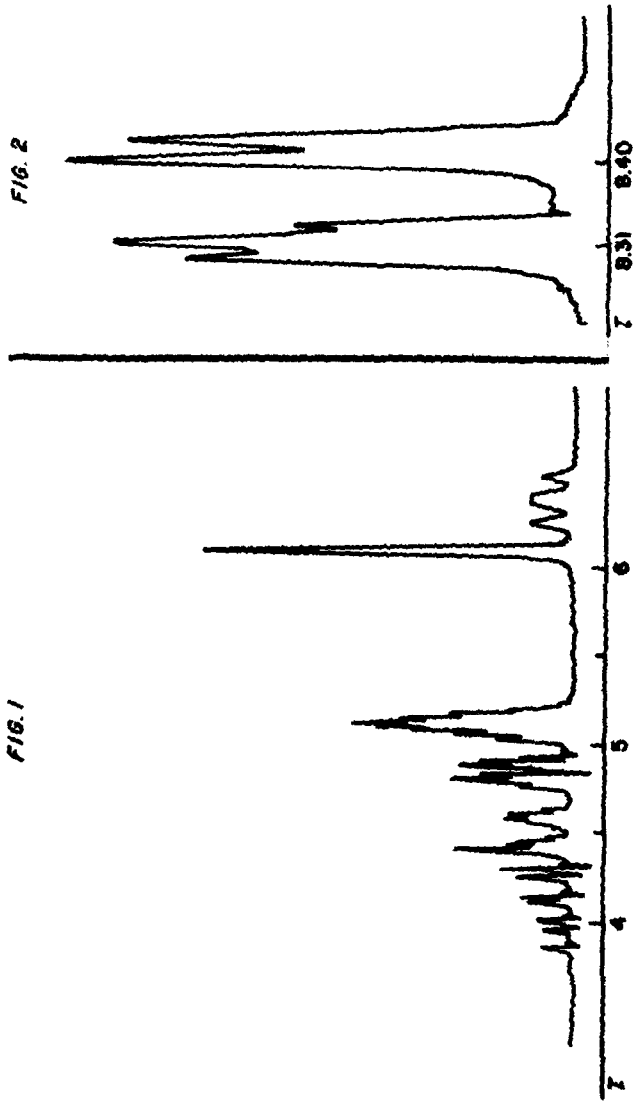
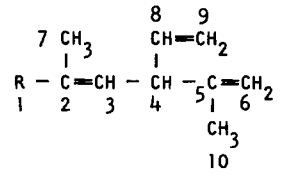


FIG. 2
8.40
8.31
τ
FIG. 1
6
5
4
τ

alcohols undergo a downfield shift of 5-10 cps when TAI is added. Upon the addition of TAI to lyratol, most of the peaks in the olefinic region were shifted slightly upfield whereas the complex signal corresponding to one proton centered at $\tau$ 4.50 moved downfield by 5 cps. This observation suggested that lyratol contains the functional group $HOCH_2 - \underset{|}{C}{=}CH -$ and the olefinic proton in this group resonates at $\tau$ 4.50 .

Further information was obtained by recording the N.M.R. spectrum of lyratol at a sweep-width of 100 cps (see Fig. 2). The two methyl signals were now clearly resolved: one as a doublet and the other as an unsymmetrical triplet, providing evidence for the non-equivalence of the two methyl groups. Therefore, the gem-dimethyl structure $(CH_3)_2C{=}CH -$ was absent.

The splitting pattern (doublet, J = 1.3 cps) of the methyl peak at $\tau$ 8.40 indicated the structural feature $CH_3 - C{=}CH -$ . The contour of the methyl signal at $\tau$ 8.31 signified allylic coupling to two protons ($J_1 + J_2 \sim 2.4$ cps ), the following structural moiety appeared most likely: $CH_3 - C{=}CH_2$ . Since these two double bonds account for only three of the six olefinic protons, a vinyl group must also be present. To accommodate the structural features deduced so far and the lack of conjugation of the double bonds, the only structure that can be derived for lyratol is 2,5-dimethyl-4-vinyl-2,5-hexadienol (I).



I R = $CH_2OH$

II R = $CH_3$

Double resonance experiments aided in substantiating the proposed structure I. The doublet signal of the $C_7$ methyl protons coalesced to an enhanced singlet when olefinic protons about 220 cps downfield were irradiated. The one proton multiplet centered at $\tau$ 4.50 must therefore correspond to the proton at $C_3$ ; this observation is in accord with the conclusions drawn from the changes in the N.M.R. spectrum of I on addition of TAI. The methyl triplet at $\tau$ 8.31 collapsed when protons that were about 180 cps downfield were irradiated. The methylene protons at $C_6$ which are coupled with the $C_{10}$ methyl protons are therefore represented by the multiplet near $\tau$ 5.15 .

The triply allylic proton at $C_4$ resonates at an appropriately low field ($\tau$ 6.4) and shows evidence for two vicinal couplings (J = 6.5 cps and 9.0 cps approx.). The peaks are broadened by allylic couplings as is to be expected for the structure I. The olefinic proton at $C_3$ exhibited a doublet of sextets which can be accounted for by a vicinal coupling (J = 6.5 cps) with the $C_4$-proton and allylic coupling with five nearly equivalent protons. An eight line, one-proton signal observed at $\tau$ 3.8 - 4.4 can be assigned to the olefinic proton at $C_8$. The two protons at $C_9$ display a multiple line complex pattern at $\tau$ 4.7 - 5.1. The different couplings deduced on the basis of first order analysis of the spectrum are shown in Table 1.

TABLE 1

Coupling Constants

| Coupled protons at | J, cps |
|---|---|
| $C_1$ , $C_3$ | 1.0 |
| $C_3$ , $C_4$ | 6.5 |
| $C_3$ , $C_7$ | 1.3 |
| $C_4$ , $C_8$ | 9.0 |
| $C_8$ , $C_9$ (trans) | 18 |
| $C_8$ , $C_9$ (cis) | 10 |
| $C_9$ , $C_9$ (gem) | 2 |
| $C_{10}$ , $C_6$ | $\left(\frac{2.4}{J_{cis} + J_{trans}}\right)$ |

The mass spectrum showing strong peaks at M-15, M-18, M-31 ($CH_2OH$) agrees with structure I. The molecular ion peak was weak as might be expected. Chemical evidence in support of structure I is provided by the observation that on hydrogenation in acetic acid in presence of platinum, lyratol consumes three moles of hyrogen. Jones' oxidation of lyratol produces a mixture of an aldehyde and an acid. The same aldehyde lyratal can also be obtained in quantitative yield by oxidizing lyratol with active manganese dioxide confirming the allylic nature of

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the alcohol. Lyratal, $C_{10}H_{14}O$, $n_D^{29}$ 1.4838, $\alpha_D^{30}$ + 37.4° (C, 3.87) shows IR bands at 2778 and 1681 $cm^{-1}$ characteristic of an αβ-unsaturated aldehyde and its UV absorption ($\lambda_{max}^{EtOH}$ 232 mμ, ε 16,390) confirms conjugation. Further chemical data and experimental details will be reported elsewhere.

Thomas and Willhalm[6] have reported the isolation of a hydrocarbon from S. Chamaecyparisus L. to which they have assigned the structure II on the basis of N.M.R. and mass spectral studies. Both structures I and II violate the isoprene rule and their biogenesis must involve some special features.[7]

## References


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