

2.00%).  $\nu_{\max}$  3050, 1720, 1655, 1620  $\text{cm}^{-1}$ . *Ellagic acid tetraacetate*, m.p. 340–341° (Found: C, 55.96; H, 3.15;  $\text{MeCO-}$ , 36.32.  $\text{C}_{22}\text{H}_{14}\text{O}_{12}$  requires: C, 56.18; H, 3.00;  $4 \times \text{MeCO-}$ , 36.57%).  $\nu_{\max}$  1780, 1745, 1610  $\text{cm}^{-1}$ . NMR: (TFA) 90MHz  $\tau$  1.7 (2H),  $\tau$  7.45 (6H,  $\text{MeCO-}$ ),  $\tau$  7.50 (6H,  $\text{MeCO-}$ ),  $\text{M}^+$   $m/e$  470.

The extract after removal of ellagic acid was chromatographed on an alumina column (Brockmann, E. Merck) to give 3,3'-*di-O-methyl-ellagic acid*, m.p. 336–338° (Found: C, 57.90; H, 3.16;  $-\text{OMe}$ , 18.23.  $\text{C}_{16}\text{H}_{10}\text{O}_8$  requires: C, 58.19; H, 3.05;  $2 \times -\text{OMe}$ , 18.78%).  $\nu_{\max}$  3200, 1725, 1610  $\text{cm}^{-1}$  superimposable with the IR of 3,3'-*di-O-methyl-ellagic acid* obtained from *E. wallichii*.

*Euphorbia wallichii*. Alcoholic extract of the roots of *E. wallichii* deposited crystals identified as 3,3'-*di-O-methyl-ellagic acid*, m.p. 335–337° (Found: C, 57.72; H, 3.1.  $\text{C}_{16}\text{H}_{10}\text{O}_8$  requires: C, 58.19; H, 3.05%).  $\nu_{\max}$  3200, 1725, 1610  $\text{cm}^{-1}$ . 3,3'-*di-O-Methyl-ellagic acid diacetate*, m.p. 300–302° (Found: C, 58.14; H, 3.20.  $\text{C}_{20}\text{H}_{14}\text{O}_{10}$  requires: C, 57.98; H, 3.41%).  $\nu_{\max}$  1760, 1605. NMR: (TFA) 90MHz  $\tau$  1.82 (2H),  $\tau$  5.58 (6H,  $-\text{OMe}$ ),  $\tau$  7.45 (6H,  $\text{MeCO-}$ ),  $\text{M}^+$   $m/e$  414.

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## DEHYDRO-1,8-CINEOLE: A NEW MONOTERPENE OXIDE IN *LAURUS NOBLIS* OIL\*

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**Key Word Index**—*Laurus nobilis*: Lauraceae; essential oil; monoterpene oxide; dehydro-1,8-cineole.

The essential oil of *Laurus nobilis* L. has been the subject of a number of investigations.<sup>1–10</sup> In each case 1,8-cineole was found to be the major component. During a recent

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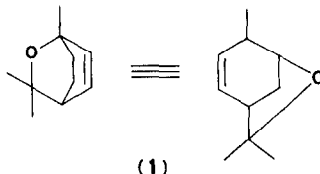
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analysis<sup>11</sup> of *L. noblis* oil an unusual compound was isolated from the lower boiling constituents. It is the purpose of this note to describe its structural elucidation. To our knowledge this is the first occasion that dehydro-1,8-cineole has been found occurring naturally.



## RESULTS AND DISCUSSION

The MS shows  $M^+ = 152$  ( $C_{10}H_{16}O$ ), loss of methyl 137 and parent ion of 109. The NMR spectrum had the following main features. Three quaternary methyl groups at  $\delta$  0.88,  $\delta$  1.17 and  $\delta$  1.23. One vinylic proton  $\delta$  5.99 (*d*) being coupled to one other proton *J* 8 Hz. Another vinylic proton  $\delta$  6.34 (*d*  $\times$  *d*) coupled to the previously mentioned vinylic proton *J* 8 Hz and the only methine proton *J* 7 Hz. The above data together with the IR data (see Experimental) suggest structure 1 for dehydrocineole. This was confirmed when cineole was found to be the sole product of hydrogenating dehydro-1,8-cineole. It is generally accepted that  $\alpha$ -terpineol is the biosynthetic precursor of 1,8-cineole. As 1,8-cineole is the major constituent of *Laurus noblis* oil it would require some dehydrogenase at the site of essential oil synthesis to product dehydro-1,8-cineole. If this were the case then it would be the first example of a loss of hydrogen from a terpene oxide during essential oil biosynthesis. Dehydro-1,8-cineole could also be formed in the plant by dehydration of 5- or 6-hydroxy 1,8-cineole or 5 or 6-hydroxy  $\alpha$ -terpineol. The latter route seems more likely in light of the biosynthetic route to 1,8-cineole.

## EXPERIMENTAL

**Oil removal and analysis.** The essential oil of *Laurus noblis* was obtained by steam distillation. After normal vacuum fractionation and chromatography over alumina<sup>12</sup> of the lower boiling components, the title compound eluted in fractions just prior to, and including those containing 1,8-cineole. Dehydro-1,8-cineole was finally isolated (~90%) from mixed fractions by careful preparative GC over SF96 and Carbowax 6000.

**Spectroscopy.** The IR spectrum, which was run as a neat film (0.13 mm spacer) between salt plates on a Beckman IR-8 had the following characteristics:  $\mu$ -3.28 medium, 3.32-3.5 strong, 6.2 weak, 6.9 m, 7.27-7.38 s, 7.55 w, 7.63 m, 7.70 m, 7.95 w, 8.11 s, 8.27 m, 8.40 m, 8.48 m, 8.62 m, 8.73 s, 9.00 s, 9.33 s, 9.71 w, 10.18 s, 10.48 s, 10.62 s, 11.03 m, 11.48 m, 11.90 s, 12.30 w, 13.01 m, 14.21 s, 14.82 m and 15.38 w. The NMR spectrum was run as a 1% soln in  $CCl_4$  on a Varian Aerograph 220 MHz spectrometer. The MS was run on a Varian Aerograph EM 600 mass spectrometer.

**Hydrogenation.** 5.4 mg of dehydro-1,8-cineole consumed 0.75 ml  $H_2$  in 5 min using Adams catalyst in AcOH. (1 equivalent = 0.8 ml  $H_2$  per double bond). Dual column capillary GC of reaction mixture showed only one peak, the IR of which was identical to 1,8-cineole.

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