

### 537. *Autoxidation of Limonene*

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THE effect of air and oxygen on limonene has been extensively studied. *trans*-Carveol and carveone were first isolated<sup>1</sup> from this reaction. Later *trans-p*-menth-8-ene-1,2-diol,<sup>2,3</sup> limonene-1,2-epoxide,<sup>3</sup> limonene-8,9-epoxide, *cis*- and *trans-p*-mentha-2,8-dien-1-ol,<sup>4,5</sup> *cis*-carveol,<sup>4</sup> and unidentified alcohols<sup>4,6</sup> were reported.

In our work (+)-limonene (200 lb.), of high purity, obtained from West Australian orange oil, was allowed to oxidise during the Australian summer in partly open steel drums and then steam-distilled. Carvone was removed by washing the distillate with a solution of sodium sulphite and sodium hydrogen carbonate, and the remaining oil was distilled. The fraction b. p. 75°/2 mm.,  $d_4^{20}$  0.9659,  $[\alpha]_D^{20}$  +20.7°,  $n_D^{20}$  1.4926, consisted largely of alcohols of formula  $C_{10}H_{18}O$  as shown by acetylation. This fraction (3 kg.) was separated into 48 fractions on a packed column (120 cm. long), giving all the terpenoids named above, but in addition perilla alcohol (75 g.), b. p. 78—80°/2 mm.,  $d_4^{20}$  0.9633,  $[\alpha]_D^{20}$  +85.2,  $n_D^{20}$  1.4991, was isolated from fractions containing carveols. Its optical rotation agreed well with that previously quoted.<sup>7</sup> Its infrared spectrum was identical with that of an authentic specimen. Its gas chromatogram showed few impurities. The alcohol was oxidised with chromium trioxide to perilla aldehyde, the semicarbazone of which had m. p. and mixed m. p. 195—196°.

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