## Synthesis of a New Tautomer of Diosphenol (Buccocamphor)<sup>†</sup>

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The monoterpenoid diosphenol (buccocamphor) has been found in the essential oil of various Barosma or Mentha species<sup>1)</sup> as crystalline, mp  $83^{\circ}$ C. The structure of this compound was established as 2-hydroxy-*p*menth-1-en-3-one **1** by F. W. Semmler and C. E. McKenzie.<sup>2)</sup> This structure was confirmed further by its synthesis from menthone<sup>3)</sup> and later by IR spectroscopy.<sup>4)</sup>

Diosphenol belongs to one of the cyclic 1,2-diketone and it is expected that this compound exists as a mixture of two enolate form; however, it has been believed that diosphenol existed only as the state, 1 shown in Fig.  $1,^{2\sim4}$ 



We now succeeded in isolating a new tautomer of diosphenol, **3** accompanied in the course of the synthesis of **1**.

(-)-Menthone was oxidized with ferric chloride in dioxane according to the method of A. K. Macbeth and W. G. P. Robertson,<sup>3)</sup> and the resulting dark red oily product was crystallized from methanol. The crystals thus obtained have melting point of  $82 \sim 3^{\circ}C$  and its structure was confirmed to be 1 by comparing the IR and NMR spectra with those of the authentic sample. On the other hand, the filtrate was evaporated to afford a red oil, which was chromatographed on silica gel column with benzene. The eluate gave a pale yellow oil, and gas chromatogram of this oil revealed the presence of two main peaks which attributed to 3 (tR, 4.5 min) and 1 (tR, 5.5 min); (SE-30-1m,  $120^{\circ}$ ;  $N_2$ , 1.2 kg/cm<sup>2</sup>). The ratio of the two components was about 4 (3): 1 (1). This mixture was subjected to the preparative glc; SE-30 column (1  $\times$  200 cm), carrier gas (N<sub>2</sub>, 60 ml/min), and the former component 3 was obtained as colorless oil of a characteristic odor, which showed a single spot in GLC and TLC.

This compound is shown to have  $M^+$  168, corresponding to  $C_{10}H_{16}O_2$  and it is partly converted to the crystalline diosphenol 1 on heating above 100°C or in the course of aluminum column chromatography. From these facts above mentioned, it is found that the structure of this compound resembles very closely to 1. This compound has hydroxyl group and the conjugated ketone group;  $\nu_{max}^{F1Im}$  3420, 1670, 1640 cm<sup>-2</sup> and its IR spectrum resembles to that of the crystalline diosphenol 1 so closely except the finger print region. UV spectrum is also similar to that of 1;  $\lambda_{max}^{MeOH}$  278 nm ( $\varepsilon$  10000).

The NMR spectrum of this compound is presented in Fig. 2. Observed signals are as follows:  $\delta_{ppm}^{CC1_4}$  1.00 (d, 3H), 1.01 (d, 3H), 1.13 (d, 3H), 1.85 (m, 2H), 2.30 (m, 3H), 3.07 (heptet, 1H), 6.00 ppm (br. s. 1H).



FIG. 2. NMR Spectrum of Iso-diosphenol, 3 (CCl<sub>5</sub>).

The characteristic signal due to  $H_8$  appears at 3.07 ppm (heptet) and there is no methyl signal adjacent to C=C bond (1.80 ppm), which is observed in the NMR spectrum of 1. From these facts the structure of the compound now obtained is concluded as 3-hydroxy-*p*-menth-2-en-2-one, 3.

This is the first report dealing with the new tautomer of diosphenol undoubtedly. We propose to name isodiosphenol to this new tautomer, 3.

## REFERENCES

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<sup>†</sup> Studies on the Isomerization of Terpenoids. Part I.