BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3591 (1969)

Two Phenol Ethers and an Aliphatic Ketone of the Essential Oil of the Kusunoki (*Cinnamomum camphora,* Sieb.)

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(Received April 30, 1969)

In previous papers,[1,2] the constituents of the sesquiterpene fraction of commercial camphor blue oil were reported. A continuous investigation of the sesquiterpene alcohol fraction was attempted more precisely. Three compounds, 2-pentadecanone, 2,3-methylenedioxynaphthalene, and piperonyl acrolein, were newly obtained in small amounts.

Experimental

The sesquiterpene alcohol fraction (bp 120—160°C/4 mmHg, 456 g) of commercial camphor blue oil was fractionated and divided into 19 fractions.

2-Pentadecanone. Fraction 5 (bp 124—126°C/4 mmHg) was chromatographed on silica gel with chloroform. White crystals were isolated from the first eluate and recrystallized (mp 35—37°C, GC pure) from ethanol. This melting point corresponds to that of 2-pentadecanone.[3] The IR spectrum indicated that this compound was an aliphatic ketone having a CH_3-CO-CH_2-group ($\nu_{C=O}$ 1710, $\delta_{CH_2-C=O}$ 1405 and $\delta_{CH_3-C=O}$ 1355 cm^{-1}). The main peaks (*m/e* 43 $(CH_3\text{-}CO)^+$, 58 (base peak) $(CH_3\text{-}CO\text{-}CH_2+H)^+$, 59 $(CH_3\text{-}CO\text{-}CH_2+2H)^+$, 71 $(CH_3\text{-}CO\text{-}CH_2\text{-}CH_2)^+$, 85 $(CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_2)^+$ and 226 M^+) were observed in the mass spectrum. From the above evidence, this compound can be said to be 2-pentadecanone.

2,3-Methylenedioxynaphthalene. From the second eluate group, white crystals were obtained and sublimed; mp 96—97°C (TLC pure). The UV spectra of this compound and naphthalene were similar to each other; the first band had the absorption maximum at λ_{max}^{EtOH} 227 mμ (ε 35000); the second band had the fine structure at 266 mμ (ε 3500), 275 mμ (ε 3700) and 286 mμ (ε 3100), and the third band at 313 mμ (ε 1900) and 325 mμ (ε 2300) showed a bathochromic shift in comparison with that of naphthalene. These bands indicated that this compound had the skeleton of β-substituted naphthalene. Moreover, this UV spectrum was much the same as that of 2-methyl-6,7-methylenedioxynaphthalene.[4] The IR spectrum showed the existence of the condensed aromatic nucleus ($\nu_{C=C}$ 1610, $\nu_{C=C}$ 1490 and $\nu_{C=C}$ 1470), the 1,2,4,5-tetrasubstituted benzene ring (δ_{CH} 857 cm^{-1}), and the methylenedioxy group (ν_{CH_2} 2790, $\nu_{=C-O-C}$ 1264, $\nu_{=C-O-C}$ 1049 and ν_{-O-CH_2-O-} 947 cm^{-1}). Therefore, the methylenedioxy group combines with naphthalene at the 2,3-positions. The mass spectrum showed peaks of *m/e* 14, 28, 44, 114, and 172 (base peak) M^+; molecular formula $C_{11}H_8O_2$ was deduced from $p+1$ (12.01%) and $p+2$ (1.20%) against M^+ (100%).[5] From the above evidence, this compound was determined to be 2,3-methylenedioxynaphthalene.

Piperonyl Acrolein. Fraction 9 (bp 132—134°C/4 mmHg) was chromatographed on alumina III with benzene. Pale yellow crystals were isolated from the middle eluate and recrystallized (mp 84—85°C, TLC pure) from ethanol This melting point corresponds to that of piperonyl acrolein.[6] The IR spestrum showed the existence of the 1,2,4-trisubstituted benzene ring (δ_{CH} 818 and δ_{CH} 877 cm^{-1}), the methylenedioxy group (ν_{CH_2} 2785, $\nu_{=C-O-C}$ 1267, $\nu_{=C-O-C}$ 1040 and ν_{-O-CH_2-O-} 932 cm^{-1}) combined with the aromatic nucleus, and the -CH=CH-CHO group (ν_{CH} 2821, ν_{CH} 2707, $\nu_{C=O}$ 1665, $\nu_{C=C}$ 1618, $\nu_{C=C}$ 1595 and δ_{CH} 975 cm^{-1}). The NMR spectrum showed the signals of aromatic protons at 6—8 ppm (3H, m, AB_2 type), methylene protons of the methylenedioxy group at 6.02 ppm (2H, s), olefinic protons of the *trans* disubstituted double bond at 7.39 ppm (1H, d, $J=16.0$ cps) and 6.53 ppm (1H, d-d, $J=16.0$ and 8.0 cps), and the aldehyde proton at 9.66 ppm (1H, d, $J=8.0$ cps). The mass spectrum showed peaks of *m/e* 147 $(M\text{-}CHO)^+$, 175 $(M\text{-}H)^+$, and 176 (base peak) M^+. Judging the above evidence, this compound is a derivative of benzene which combines with the methylenedioxy group at the 1,2-positions and with the -CH=CH-CHO group at the 4-position. Thsu, this compound can be said to be piperonyl acrolein.

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1) S. Hayashi, N. Hayashi, K. Yano, M. Okano and T. Matsuura, This Bulletin, **41**, 234 (1968).

2) S. Hayashi, K. Yano, N. Hayashi and T. Matsuura, *ibid.*, **41**, 1465 (1968).

3) P. Baumgarten, *Ber.*, **76**, 213 (1943).

4) C. Tani, N. Takao and K. Tagahara, *Yakugaku Zasshi*, **84**, 1217 (1964).

5) J. H. Beynon, "Mass Spectroscopy and Its Application to Organic Chemistry," Elsevier Amsterdam (1960).

6) T. Ikeda, S. Takeda, H. Nakama and T. Yokohara, *Nippon Kagaku Kwaishi (J. Chem. Soc. Japan)*, **61**, 583 (1940).