Natural Occurrence of Humulol and Tricyclohumuladiol

Yoko NAYA and Munio KOTAKE

The Institute of Food Chemistry, Dojimanaka, Kita-ku, Osaka

(Received June 11, 1969)

In our series papers[1] we have reported new constituents of hop oil. This communication will deal with two sesquiterpene alcohols, humulol (I) and tricyclohumuladiol (II), isolated from the same source.

The alcohol (I) is a viscous oil, $C_{15}H_{26}O$, $[\alpha]_D^{24}$ $-1.2°$ (c=0.87, MeOH), which exhibited hydroxyl group absorptions (3370 and 1110 cm^{-1}) in the IR spectrum. The other characteristic absorption bands were shown at 1380, 1365 (*gem*-dimethyl), and 980 cm^{-1} (C=C *trans*). The IR and NMR spectra of the compound I were identical with those of the alcohol, which had been isolated by Buttery *et al.*[2] They suggested[3,4] that the alcohol might be the same as Chapman's luparenol,[5] also isolated from hop oil; this suggestion was made on the basis of the molecular formula, $C_{15}H_{24}O$. If the two are the same, the molecular formula must be corrected. However, the identity of the compound (I) and "luparenol" can not be confirmed because of insufficient evidence. To avoid confusion, therefore, we propose the name "humulol" for the compound (I).

Its NMR spectrum[*1] showed two singlets, at 1.05 and 1.10 (each 3H), and a doublet at 1.59 (3H, J=1 Hz), due to tertiary methyl groups and a vinyl methyl group respectively; and a singlet at 1.15 (3H) assignable to a methyl attached to a carbon atom bearing a hydroxyl group; complex multiplets located between 4.90—5.20 account for three vinyl protons (HC=CH and $CH=CCH_3$). The mass spectrum exhibited its molecular ion peak at m/e 222 and its base peak at m/e 82.

The hydrogenation of I with PtO_2 in acetic acid gave the saturated compound, $C_{15}H_{30}O$ (M^+, m/e 226).

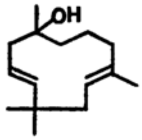
When the alcohol (I) was injected in a preparative GLC (SF-96) at 220°C, the greater part of it was converted into β-humulene, which was identical with the authentic compound (IR, NMR, and MS). The above evidence indicates the structure I for humulol.

The diol II, named tricyclohumuladiol, $C_{15}H_{26}O_2$, $[\alpha]_D^{24}$ 0° (c=2.7, MeOH), was recrystallized from methanol-ether as colorless plates; mp 207°C. II exhibited hydroxyl absorptions (3300, 1135 cm^{-1}) and bands (1010, 895 cm^{-1}) assignable to cyclopropane ring in the IR spectrum; other peaks of diagnostic value were at 1360 and 1375 (*gem*-dimethyl). Its NMR spectrum ($(CD_3)_2SO$) showed singlets at 0.89, 0.95, 0.96, and 1.03 (each 3H, tertiary methyls); a multiplet centered at 2.98 (1H) is assignable to a proton on the carbon atom bonded to a hydroxyl group; a complex multiplet located between 0.10—0.70 accounts for three protons on a cyclopropane ring. The mass spectrum exhibited its molecular ion peak at m/e 238 and its base peak at m/e 43.

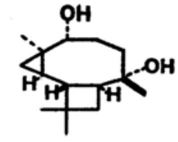
On acetylation with acetic anhydride and pyridine, II gave a monoacetate (III), $C_{17}H_{28}O_3$ (M^+, m/e 280), mp 69—70°C (rhombic). Upon treatment with $SOCl_2$-pyridine or hydrochloric acid in a methanol solution, a tertiary hydroxyl group of III was replaced by chlorine; yielded was a viscous oil (IV), $C_{17}H_{27}O_2Cl$, which did not exhibit any hydroxyl absorption in its IR spectrum.

When II was oxidized with CrO_3-pyridine, it afforded a hydroxy-ketone (V), $C_{15}H_{24}O_2$, which could be purified by GLC. The IR and UV spectra indicated that V is a macro-cyclic ketone conjugated with a cyclopropane ring (1670 cm^{-1} (C=O); λ_{max}^{hexane} 203 mμ (ε 2800)). V was characterized as a chloro-compound (VI), $C_{15}H_{23}OCl$, mp 115—116°C, by the method described above.

The chemical properties and physical constants of the diol (II) were quite simiar to those of the authentic compound[6] prepared from humulene; the absolute conformation is shown as the formula (II).



I



II

---

[1] Previous paper: Y. Naya and M. Kotake, This Bulletin, **42**, 2088 (1969).

[2] R. G. Buttery, W. H. McFadden, R. E. Lundin and M. P. Kealy, *J. Inst. Brew.*, **70**, 396 (1964).

[3] R. G. Buttery and L. C. Ling, *Brewers Digest*, **1966**, 71.

[4] R. G. Buttery, R. E. Lundin and L. Ling, *Agri. Food Chem.*, **15**, 58 (1967).

[5] A. C. Chapman *J. Chem. Soc.*, **1928**, 1303.

[*1] All NMR spectra were taken in CCl_4 on a JEOL Model C-60 spectrometer with TMS as an internal reference. The values are reported in ppm.

[6] J. M. Greenwood, M. D. Solomon, J. K. Sutherland and A. Torre, *J. Chem. Soc., C*, **1968**, 3004.