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A NEW CONSTITUENT OF HOP OIL

Y. Naya and M. Kotake

The Institute of Food Chemistry, Kitaku, Osaka, Japan

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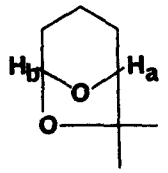
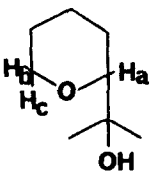
In a previous paper (1) we reported the isolation of oxetone derivatives from Japanese hop "Shinshu-wase". In the present communication, the isolation and structural determination of a new constituent, 7,7-dimethyl-6,8-dioxabicyclo [3,2,1]octane (I), from the same source is described.



I



II

The compound (I), $C_8H_{14}O_2$, was isolated from the fraction, boiling at 125°C/ 25.5 mm Hg, by silica gel-column chromatography and preparative gas chromatography. The other constituents of this fraction were (+)-amyl propionate and (+)-amyl isobutyrate.

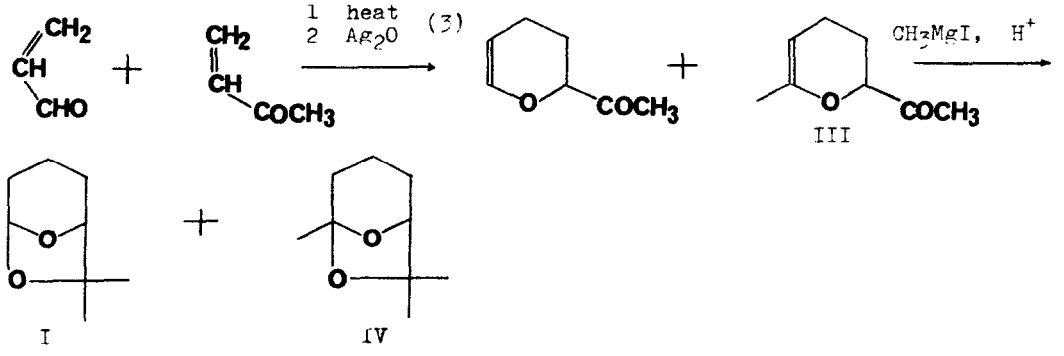
Compound (I) exhibited infrared absorptions at 1385, 1365 and a doublet in the 1120-1110 cm^{-1} region, attributable to gem-dimethy and C-O-C-O-C groups, respectively. The mass spectrum (M^+ion at m/e 142) showed a base peak at m/e 84 due to expulsion of C_3H_6O. Its nmr spectrum (in CCl_4) shows signals assignable to two methyls at 1.19 (3H s.) and 1.36 (3H s.), methylenes at ca. 1.55 (6H multiplet) and two protons linked to the carbons bonded to the oxide linkage at 3.70 (1H, broad s., H_a) and 5.33 ppm (1H, broad s. H_b).

Reduction of the compound (I) with lithium aluminum hydride-aluminum chloride (2) yielded the ring-opened product (II), $C_8H_{16}O_2$ (MS: M^+ion m/e 144, base peak

m/e 85), which showed an infrared absorption band due to a hydroxyl group.

The nmr spectrum of (II) showed the presence of two methyls at 1.05 (6H s.), methylenes at ca. 1.50 (6H multiplet), hydroxyl proton at 2.25 (1H s.) and three protons attached to the carbons bearing the oxide linkage at 3.00 (1H, broad d., H_c-axial), 3.48 (1H, multiplet, H_b-equatorial) and 4.00 ppm (1H, broad d., H_a).

(I) was identical with an authentic sample which was prepared, together with the compound (IV), as follows:



Compound (IV), $C_9H_{16}O_2$ was resulted from the selfcondensation product (III) of methyl vinyl ketone. It exhibits the following spectroscopic properties, MS: M^+ion at m/e 156 and base peak at m/e 43; nmr: 1.19 (3H s.), 1.30 (6H s.), ca. 1.57 (6H multiplet), 3.70 ppm (1H broad s.).

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