

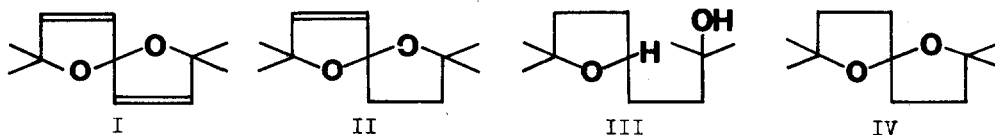
THE ISOLATION OF NEW OXETONE DERIVATIVES FROM HOP OIL

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This paper deals with the first isolation of oxetone derivatives from natural sources and the determination of their structures as 2,2,7,7-tetramethyl-1,6-dioxaspiro[4,4]-nona-3,8-diene (I) and 2,2,7,7-tetramethyl-1,6-dioxaspiro[4,4]-non-3-ene (II).



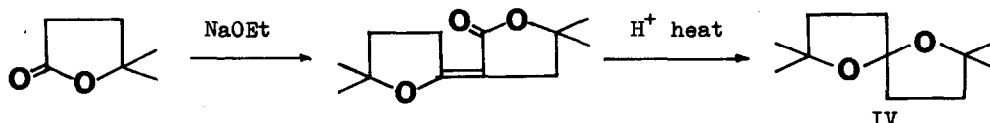
the oxetone derivatives (I), $C_{11}H_{16}O_2$ (MS: M^+ ion m/e 180) and (II), $C_{11}H_{18}O_2$ (MS: M^+ ion m/e 182) were isolated from the fraction, boiling at $82^\circ C/12$ mm Hg, of the steamdistilled oil from Japanese hop "Shinshu-wase" cropped 1963 in Yamagata Pref. by silica gel-column chromatography and preparative gas chromatography. Another ingredient of this fraction was (+)-amyl-isobutyrate.

The oxetone derivatives (I) and (II) exhibited infrared absorptions at 1620, 1280 and four bands in the $1200-1000\text{ cm}^{-1}$ region, attributable to double bond and spiroketal groups, respectively. The nmr spectrum of (I) showed a pair of doublets ($J=5$ cps) at 5.89 and 5.40 ppm corresponding to olefin protons (4H). In the methyl signal region, there were two singlets at 1.33 and 1.26 ppm, ascribable to methyl groups attached to the carbons bearing an oxide linkage. The nmr spectrum of (II) suggested that it corresponded to a dihydro derivative of (I), since the intensity of signals at 5.84 (d. $J=5$ cps) and 5.39 ppm (d. $J=5$ cps) corresponded to two olefin protons and a multiplet arising from four methylene

protons was observed at 2.0-1.86 ppm. The signals at 1.30 (3H s.), 1.27 (3H s.), 1.20 (3H s.) and 1.11 ppm (3H s.), which could be assigned to four methyl groups attached to an oxide linkage, further supported the relationship between (I) and (II).

Hydrogenation of compounds (I) and (II) in acetic acid with platinum oxide yielded the ring-opened hydrogenation product (III), $C_{11}H_{22}O_2$ (MS: M^+ ion m/e 186), which had an infrared absorption band due to a hydroxyl group. The nmr spectrum exhibited an unresolved absorption at 1.22 ppm (12H, methyl groups), a multiplet at 3.96 ppm (1H, proton α to the oxide linkage) and a singlet at 2.7 ppm (1H, hydroxyl proton). The methylene protons absorbed as a multiplet (8H) in the region of 1.82-1.57 ppm. On the other hand, the hydrogenation of (I) and (II) by the same catalyst in ether gave the saturated spiro compound (IV), $C_{11}H_{20}O_2$ (MS: M^+ ion m/e 184) and a small amount of (III). The methyl groups were observed in the nmr spectrum at 1.30 (6H s.) and 1.13 (6H s.), while the methylene protons absorbed at 1.93-1.60 ppm (8H multiplet).

(IV) was found to be identical with authentic tetramethyloxetone which was prepared (1,2) from isocaprolactone by the following reactions.



REFERENCES

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