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9-OXONEROLIDOL FROM CAMPHOR LEAF OIL

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9-Oxonerolidol was obtained from the nonvolatile fraction of the leaf oil of camphor tree. Its constitution was determined by means of spectal and chemical analyses.

The constituents of the volatile oil of the leaves collected from one kind of camphor tree (sesquiterpene tree [1]) were previously reported.[2,3]

We wish to report here that 9-oxonerolidol, which has not been found in nature, was obtained as a major component of the nonvolatile terpenoids in the leaf oil of the sesquiterpene tree.

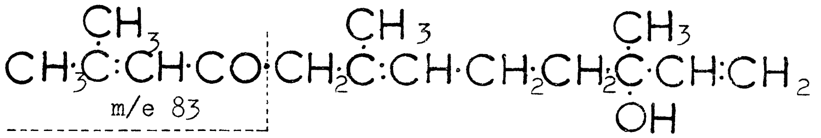
The leaves were extracted with acetone, and the extract was treated with n-hexane after concentration. From the hexane solution, the solvent was removed off, and the residue was steam distilled, the distillate weighing about 0.5 % per leaves. The remaining material was dissolved in n-hexane and chromatographed on a column of neutral alumina with hexane-ethyl acetate (85:15) to give 31 fractions. The main component (I), which was obtained from the fractions 13-30, was purified by means of TLC using silica gel to afford a liquid; $C_{15}H_{24}O_2$, m/e 236 (M^+), 221 (M^+-15), 218 (M^+-18), 83 (base peak); $[\alpha]_D +15.38^\circ (CCl_4)$, n_D^{20} 1.4982; UV: λ_{max} 238mμ ($\varepsilon=1.1 \times 10^4$) in hexane; IR: 3400, 1150cm^{-1} (tert. alcohol), 995, 930cm^{-1} (vinyl), 1660, 1620cm^{-1} (α,β-unsaturated ketone); NMR: 1.30ppm (3H,s, $C\underline{H}_3-\overset{|}{\underset{|}{C}}-OH$), 1.60ppm (3H,s, $>C=\overset{|}{C}-C\underline{H}_3$), 1.88ppm (3H,s), 2.15ppm (3H,s) ($(C\underline{H}_3)_2C=\overset{|}{C}-\overset{|}{C}=O$), 3.03ppm (2H,s, $O=C-C\underline{H}_2-\overset{|}{C}=C<$), 4.90-5.40ppm (3H, $-CH=C\underline{H}_2$, $>C=C\underline{H}-$), 5.93ppm (1H,dd, J=17 and 10.5cps, ■$-C\underline{H}=CH_2$; ■ indicates carbon with no proton), 6.09ppm (1H, br.s, $>C=C\underline{H}-\overset{|}{C}=O$).

(I) was hydrogenated with Pd-C in methanol; 3.45 moles of hydrogen were absorbed per one mole of (I). The product was separated into two components (II,III) by means of TLC using silica gel. (II) was a saturated ketone; $C_{15}H_{30}O$, m/e 226 (M^+), 169 (M^+-57), 85 (M^+-141), 28 (base peak), IR: 1720cm^{-1}, NMR: 0.8-1.0ppm (15H, $5C\underline{H}_3$), 2.1-2.3ppm (4H, $-C\underline{H}_2-CO-C\underline{H}_2-$). This hydrogenolysis of hydroxyl group indicates that hydroxyl group in (I) is allylic. (III) was a hydroxyketone; $C_{15}H_{30}O_2$ m/e 227 (M^+-15), 224 (M^+-18), 213 (M^+-29), 85, 28 (base peak), IR: 3400, 1150cm^{-1} (tert. alcohol), 1710cm^{-1} (ketone), NMR: 0.8-1.0ppm (12H, $4C\underline{H}_3-$), 1.10ppm (3H,s, $C\underline{H}_3-\overset{|}{C}-OH$), 2.15-2.35ppm (4H, $-C\underline{H}_2COC\underline{H}_2-$).

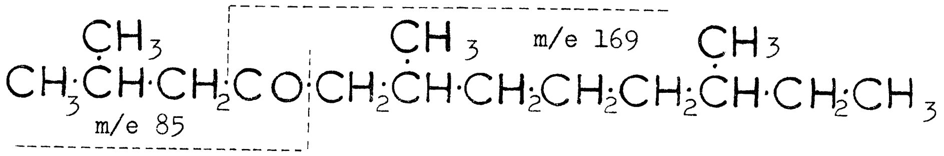
(I) was reduced with sodium borohydride in methanol to give (IV). (IV) was a diol; IR: 3400, 1150cm^{-1} (tert. alcohol), 1050cm^{-1} (sec. alcohol), 915, 995cm^{-1} (vinyl); NMR; 1.20ppm (3H,s, $C\underline{H}_3-\underset{|}{\overset{|}{C}}-OH$), 1.60-1.75ppm (9H, $C\underline{H}_3-\underset{|}{C}=C\lessdot$), 4.30ppm (1H,m,$-C\underline{H}OH-$), 4.90-5.35ppm (4H, $>C=C\underline{H}-C-OH$, $>C=C\underline{H}-$, $-CH=C\underline{H}_2$), 5.83ppm (1H,dd, J=18 and 10.5cps, $-C\underline{H}=CH_2$). (IV) was supposed to be a mixture of stereoisomers from the finely splitting signals especially in the region near 5.83ppm but they could not be separated by means of TLC using silica gel.

From the mass spectral data of (I)[m/e 83], (II)[m/e 85 and m/e 169] and (III) [m/e 85], the position of carbonyl carbon can be determined.

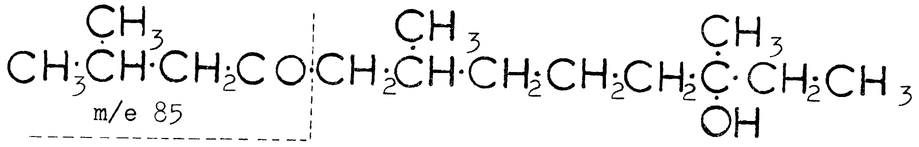
From these ground (I) was identified as 9-oxonerolidol.


$CH_3\overset{CH_3}{C}{:}CH\cdot CO\cdot CH_2\overset{CH_3}{C}{:}CH\cdot CH_2CH_2\underset{OH}{\overset{CH_3}{C}}\cdot CH{:}CH_2$

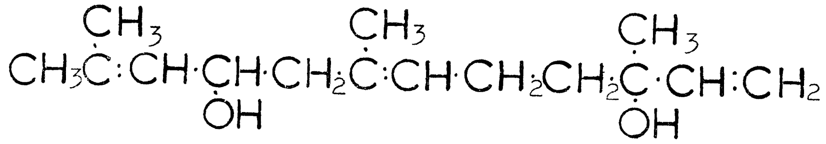
(I)


$CH_3\overset{CH_3}{CH}\cdot CH_2CO\cdot CH_2\overset{CH_3}{CH}\cdot CH_2CH_2CH_2\overset{CH_3}{CH}\cdot CH_2CH_3$

(II)


$CH_3\overset{CH_3}{CH}\cdot CH_2CO\cdot CH_2\overset{CH_3}{CH}\cdot CH_2CH_2CH_2\underset{OH}{\overset{CH_3}{C}}\cdot CH_2CH_3$

(III)


$CH_3\overset{CH_3}{C}{:}CH\cdot\underset{OH}{CH}\cdot CH_2\overset{CH_3}{C}{:}CH\cdot CH_2CH_2\underset{OH}{\overset{CH_3}{C}}\cdot CH{:}CH_2$

(IV)

References

1) N. Hirota: Mem. Ehime Univ. Sect. II, Vol.1, No.2, 1(1951)
2) N. Hirota & M. Hiroi: The Koryo, No.70, 23(1963)
3) M. Hiroi: Bull. Chem. Soc. Japan 40 2689(1967)

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