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THE STEREOSTRUCTURE OF CHILOSCYPHONE[1)]

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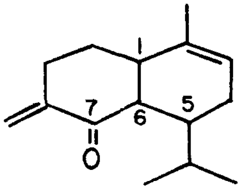
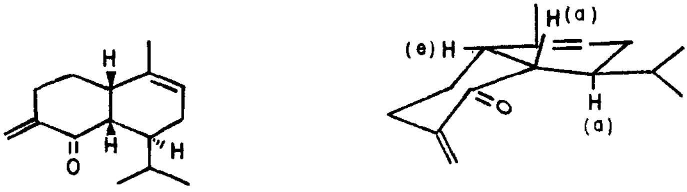
In a previous communication[2)] we have presented the name chiloscyphone for a main component of an essential oil obtained from Chiloscyphus polyanthus (L.) Corda, Japanese name Fujiurokogoke, which is placed in the class Hepaticae (Harpanthaceae), and elucidated the structure to be a cisoidal α,β-unsaturated ketone, 2-methyl-5-isopropyl-8-methylene bicyclohexane-7-one (formula I). This communication is concerned with evidences to show that the absolute configuration and the conformation of the ketone is represented by the non-steroidal cis-decaline type (formula II).

For the planar formula (I) containing three asymmetric centers there are eight stereoisomers of four cis- and four trans-decaline type. As to the cis-decaline type isomers, furthermore, both steroidal and nonsteroidal conformers should be respectively considered. Accordingly, the possible conformers for (I) are twelve in the total numbers.

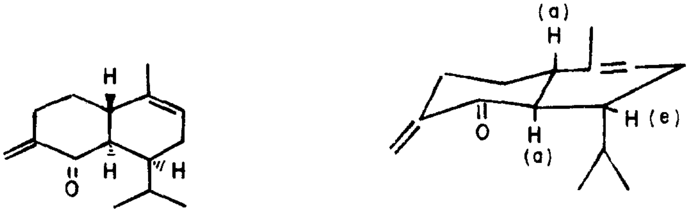
The NMR of chiloscyphone[3)] exhibited a signal due to the C_6-methyne proton, which is adujacent to the carbonyl group, at 3.59 ppm with a sharp quartet (J=6.9 and 2.0 cps). From the pattern of the spectrum it was deduced that three neighboring methyne protons on C_1, C_6 and C_5 take the conformational relation of a-a-e or e-a-a [4)]. Of the twelve stereostructures counted above, ones keeping such relation are merely four conformers of (II), (III), (IV) and (V). Regarding the R-band Cotton effect of α,β-unsaturated ketones an extended octant rule has been proposed indicating that cisoidal α,β-unsaturated ketones obey the normal octant rule[5)].



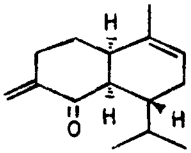
(I)



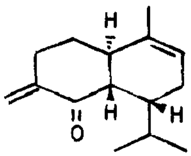
(II)



(III)



(IV)



(V)

When the molecular models were examined in a standpoint of the rule, it was ascertained that both (II) and (III) give a negative sign, and their antipodes, (IV) and (V), a positive one on ORD and CD curves. Chiloscyphone should be thus represented by either (II) or (III).

Next, tetrahydrochiloscyphone which was obtained on the hydrogenation over Adams catalyst in acetic acid exhibited a positive Cotton effect; $[\phi]_{322}$ +910, $[\phi]_{275}$ -870, a=+15.8: $[\theta]_{298}$ +9300 in Dioxane; $[\phi]_{313}$ +1140, $[\phi]_{270}$ +30, a=+11.7: $[\theta]_{299}$ +9010 in Isooctane. For all saturated ketones derived from (II) a positive sign is expected, whereas all those from (III) are expected to show a negative sign. These facts leaded us to the conclusion that chiloscyphone is reasonably represented by the nonsteroidal cis-decaline type (II).

In order to obtain an additional support ORD and CD curves in $\pi \longrightarrow \pi^*$ transition of the original ketone were determined; $[\phi]_{228}$ -13080, $[\phi]_{205}$ +91560, a=-1050: $[\theta]_{222}$ -46040 in Isooctane. This negative Cotton effect is not in contradiction to (II)$^{6)}$.

The solvent dependence ($[\theta]_{350}$ -2540 in Dioxane, $[\theta]_{356}$ -2810 in Isooctane) and the temperature dependence ($[\theta]_{350}$ -2990 at +24 °C, $[\theta]_{350}$ -3550 at -74 °C in EPA$^{7)}$) were hardly observed above the R-band CD curves of chiloscyphone. This indicates that the assigned nonsteroidal conformer having the isopropyl group in equatorial conformation is of the very great stability comparing with its inverted conformer.

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5) W. B. Whalley, Chem. Ind. (London), 1962, 1024
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7) EPA solvent is composed of ether-isopentane-ethanol in the ratio 5:5:2 by volume