

CHILOSCYPHONE, A NEW  $\alpha,\beta$ -UNSATURATED SESQUITERPENE KETONE

FROM CHILOSCYPHUS POLYANTHUS (L.) CORDA

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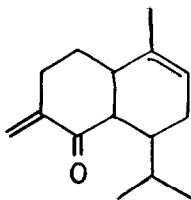
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A new sesquiterpene ketone was isolated from the essential oil of Chiloscyphus polyanthus (L.) Corda, and its structure was determined as formula I.

We propose the name chiloscyphone for this ketone, and the evidence of the proposed structure is described.



I

From the essential oil collected by steam-distillation of the whole plant the ketone was obtained in gas and thin layer chromatographically pure state by means of the fractional distillation followed by elution chromatography.  $C_{15}H_{22}O$  (calcd. m/e 218.1670, obsd. m/e 218.1676), bp 121-122 °C/2mm,  $[\alpha]_D^{25} -45.7^\circ$  (dioxane, c, 1.0%).

This compound afforded 2,4-dinitrophenylhydrazone, mp 174-175 °C, and was characterized as an  $\alpha,\beta$ -unsaturated ketone on the basis of  $\nu_{\max}^{liq}$  1629 and 1670  $cm^{-1}$  and  $\lambda_{\max}^{EtOH}$  220  $m\mu$  ( $\epsilon$  8960).

Since the ketone was dehydrogenated by heating with palladium-charcoal in a sealed tube to produce cadalene in a good yield, which was identified with IR spectrometric and gas chromatographic comparison with the authentic sample, it may be thought to have a cadalene skeleton.

The IR and NMR spectra exhibited the presence of an isopropyl ( $\nu$  1370, 1380  $\text{cm}^{-1}$ ; 0.96, 3H, s, 0.85, 3H, d,  $J=5.5$ ), an exo methylene ( $\nu$  935  $\text{cm}^{-1}$ ; 5.75, 1H, d,  $J=1.2$ , 5.96, 1H, s) whose signals shifted about one ppm from the normal region, a methyl attached to a double bond (1.83, 3H, d,  $J=1.2$ ), and a trisubstituted double bond ( $\nu$  857  $\text{cm}^{-1}$ ; 5.42, 1H, m).

The compound took up hydrogen to two moles in the catalytic hydrogenation over Adams catalyst in acetic acid to produce a saturated ketone ( $\nu$  1702  $\text{cm}^{-1}$ ) having no active methylene.

Thus, it is certain that the compound has two double bonds as an exo methylene and a trisubstituted double bond carrying a methyl group. In the catalytic hydrogenation using palladium-charcoal as a catalyst in ethanol, the original  $\alpha,\beta$ -unsaturated ketone produced a dihydro ketone ( $\nu$  1703  $\text{cm}^{-1}$ ) leaving the trisubstituted double bond ( $\nu$  850  $\text{cm}^{-1}$ ) unattacked.

The carbonyl group in chiloscyphone, therefore, is conjugated with the exo methylene double bond. Among such conjugated structures the structure I is the only one in which active methylene vanished away on catalytic hydrogenation leading to the tetrahydro ketone.

The structure of chiloscyphone was elucidated as 2-methyl-5-isopropyl- $\alpha$ -methylene bicyclo[4.4.0]dec-2-en-7-one, the structure of which is also supported by the existence of a methyne proton adjacent to a carbonyl group at 3.59 (1H, q,  $J=5.9$  and 2.0) in the NMR spectrum of the original ketone.

The elucidation of its stereochemistry will be reported later.

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