Tetrahedron Letters No.51, pp. 5315-5318, 1968. Pergamon Press. Printed in Great Britain.

ISOLATION AND STRUCTURES OF THREE NEW SESQUITERPENES

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(Received in Japan 14 August 1968; received in UK for publication 30 August 1968)

Several sesquiterpenes have been isolated from Sweet-flag oil.[1)] We have examined the sesquiterpenic components of the Rhizoma of Acorus calamus L. (Japanese name, "Shyôbu"), and could isolate three new sesquiterpenes from the volatile oil.* All of them were monocyclic ketones, having the proper odor to the original wild plant, and named Shyobunone(I), Epishyobunone(II) and Isoshyobunone(III).

The essential oil was obtained by means of steam distillation, and then the sesquiterpenic fractions were successfully separated by repeated silica gel chromatography, and finally by preparative gas-liquid chromatography. (Yields, I: 1.25%, II: 4.02%, III: 1.34% of the oil).

Three ketones were colorless liquids, all of which had the same molecular formula $C_{15}H_{24}O$. The numerical values of the specific retention vs. cyclohexanone (PEG 20M, 115°) were: I, 11.73; II, 9.79; III, 11.12. The IR ($\nu_{max.}^{film}$ 1710 and 1639 cm^{-1}) and UV ($\lambda_{max.}^{MeOH}$ 206 mμ, $\varepsilon = 3010$) spectra of I coupled with the NMR spectrum** indicated the presence of a carbonyl and two double bonds.

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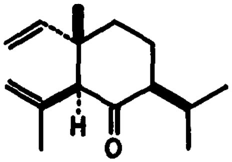
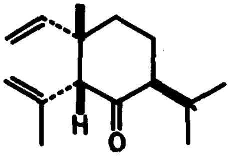
* Other compounds were also isolated. One of them seemes to be a new sesquiterpene diol.

** NMR signals were observed at 0.87 and 0.90(6H, d, J = 6.4; $\begin{matrix}C\underline{H}_3\\C\underline{H}_3\end{matrix}{>}CH-$), 1.02(3H, s; $\geq C-CH_3$), 1.76 (3H, near singlet; $H_2C{=}\underset{|}{C}-C\underline{H}_3$), 2.95(1H, s; $\geq C-H$), 4.65—5.10(4H, m; $\underline{H}_2C{=}CH-C\leq$ and $\underline{H}_2C{=}\underset{|}{C}-CH_3$), and 5.82 ppm (1H, q, J = 18, 10 cps; $CH_2{=}C\underline{H}-C\leq$), on a Varian A-60, using carbon tetrachloride as a solvent and also tetramethylsilane as an internal reference. (Abbreviations, d: doublet, m: multiplet, q: quartet, s: singlet)


I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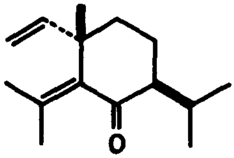
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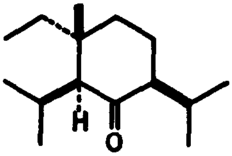
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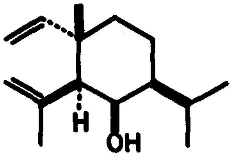
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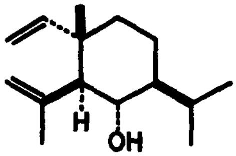
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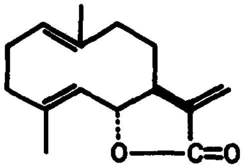
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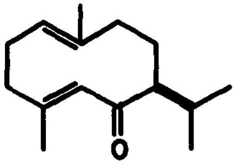
VIII

Furthermore, catalytic hydrogenation of I afforded a tetrahydro product(IV), indicating that the presence of the two double bonds in the original ketone.

When treated with lithium aluminium hydride, I gave two hydroxy compounds(V and VI) in 58.3 and 8.7% yields, respectively. From these evidences it was concluded that Shyobunone(I) was a monocyclic sesquiterpene, the structure of which was proved to be identical with 2β-isopropenyl-3β-methyl-3α-vinyl-6β-isopropyl cyclohexanone chemically transformed from costunolide(VII),[2] by IR and NMR spectra.

Epishyobunone(II) obtained from the second fraction of silica gel chromatography showed a mass spectrum very close to Shyobunone except for a peak at 192 m/e (M^+- 28), and the IR and UV spectral data of II ($\nu_{max.}^{film}$ 1710 and 1641 cm^{-1}; $\lambda_{max.}^{MeOH}$ 207 mμ, ε = 3400) as well as NMR signals at 0.85 and 0.88(6H, d, J = 6.2), 1.05(3H, s), 1.77(3H, near singlet), 3.00(1H, s), 4.72—5.07(4H, m) and 5.72 ppm (1H, q, J = 18, 10 cps) were also very similar to that of Shyobunone(I).

However, the optical rotatory dispersion curve* of II was different from that of I: the former showed a strongly negative Cotton effect ($[\phi]^{T}_{315}$ $-89° \times 10^2$, $[\phi]^{P}_{279}$ $+111° \times 10^2$, A -200) indicating that II had an axial isopropenyl group at C-2, whereas a positive Cotton effect of the latter ($[\phi]^{P}_{318}$ $+18.7° \times 10^2$, $[\phi]^{T}_{275}$ $-121° \times 10^2$, A +140) was in good agreement with the expected configuration of I.

The IR and UV spectra ($\nu^{film}_{max.}$ 1678 and 1614 cm^{-1}; $\lambda^{MeOH}_{max.}$ 252 mμ, $\varepsilon = 4180$) of Isoshyobunone (III) indicated the presence of an α,β-unsaturated cisoid ketone. In addition, NMR signals at 0.85 and 0.89 (6H, d, J = 6.4; assigned to $\begin{matrix}C\underline{H}_3\\C\underline{H}_3\end{matrix}{>}CH-$), 1.36 (3H, s; $\geq C-CH_3$), 1.75 (6H, s; $\begin{matrix}CH_3\\CH_3\end{matrix}{>}C{=}C{<}$), 4.95 (1H, q, J = 18, 1.6; $\begin{matrix}H\\\underline{H}\end{matrix}{>}C{=}C{<}^{H}$), 4.96 (1H, q, J = 9.9, 1.5; $\begin{matrix}\underline{H}\\H\end{matrix}{>}C{=}C{<}^{H}$) and 5.94 ppm (1H, q, J= 18, 10 cps; $H_2C{=}C\underline{H}-$) satisfied the structure of III.

Finally both unconjugated ketones, I and II, were converted to III, when treated with sodium methoxide or refluxed with formic acid. Furthermore, the gas-liquid chromatograms of I and II indicated that I was converted into III through the unstable epimer(II) which was considered to be

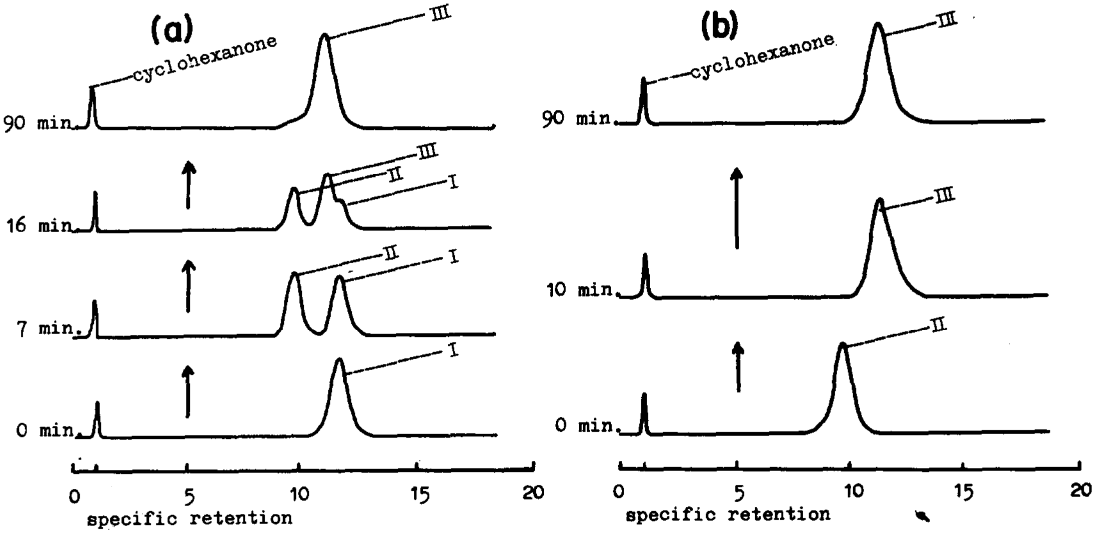

Fig. 1 Gas-liquid chromatograms, during the pyrolyses of I and II, at 280°, in a sealed tube. Stationary phase: PEG 20M(10% on Celite 545, 80—100 mesh), 115°, Carrier gas: nitrogen, 1.2 kg/cm^2, Detector: flame ionizer. Specific retention was recorded vs. cyclohexanone as an internal standard.

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* ORD curves were taken on a JASCO Model ORD/UV-5 using methanol as a solvent. Abbreviations: A, amplitude; P, peak; T, trough.

in a certain equilibrium with I, during the pyrolysis. On the other hand, II was isomerized to III more rapidly than I, and in this case the formation of the more stable epimer (I) could not be detected, as shown in Fig. 1.

From the above chemical reactions, the structural relationship among three ketones was established.

On a biogenetic point of view, however, a ten-membered monocyclic ketone (VIII) may be regarded as a precursor of these three sesquiterpenes, I, II and III, in the original plant.

We thank Drs. G.R. Kelkar and S.C. Bhattacharyya for providing us with the coppies of IR and NMR spectra of 2β-isopropenyl-3β-methyl-3α-vinyl-6β-isopropyl cyclohexanone.

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