Tetrahedron Letters No.10, pp. 1251-1254, 1968. Pergamon Press. Printed in Great Britain.

STRUCTURE OF SESQUICARENE

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(Received in Japan 8 November 1967)

Sesquicarene is a hydrocarbon isolated from the essential oil of fruits of Schisandra chinensis Baill. by combination of fractional distillation, column chromatography over silica gel impregnated with silver nitrate and preparative gas chromatography. This hydrocarbon is the second abundant component of the oil and its nomenclature is based on the structure which has an additional isoprenyl group on 2-carene.

Sesquicarene (I), $C_{15}H_{24}$, shows the following physical properties; $[\alpha]_D^{25}$ -76.9° (c, 0.82)*, ν_{max}^{liq} 1660, 1640 and 830cm^{-1}, $\lambda_{max}^{n\text{-}hexane}$ 208mμ (ε 8,800), $\delta_{ppm}^{CCl_4}$ 0.82 (3H, s., $-\overset{|}{\underset{|}{C}}-C\underline{H}_3$), 1.59 (3H, broad s., $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), 1.64 (6H, broad s., $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), 5.00 and 5.45 (each 1H, broad s., $-\overset{|}{C}=\overset{|}{C}\underline{H}$), M$^+$ion m/e 204 and base peak m/e 119.

Compound I is bicyclic with two double bonds, as, on hydrogenation with Adams' catalyst in acetic acid, it yielded a saturated tetrahydro derivative (II) ($[\alpha]_D^{25}$ +19.5°, M$^+$ion m/e 208 and base peak m/e 123). On catalytic hydrogenation using the same catalyst in acetic acid in the presence of a small amount of perchloric acid, I absorbed three molar equivalent of hydrogen to yield bisabolane (III). Thus, one of the two rings of I is cyclopropane and, therefore, the carbon skeleton of I must be a bisabolane type with a cyclopropane ring. When I was hydrogenated in ethanol using platinum oxide, it afforded

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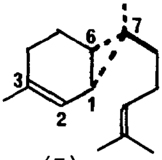
* The $[\alpha]_D$ values recorded in this communication were measured in $CHCl_3$ solution.

a dihydro derivative (IV) ($[\alpha]_D^{28}$ -69.3° (c, 0.65), $\delta_{ppm}^{CCl_4}$ 0.81 (3H, s., $-\overset{|}{\underset{|}{C}}-C\underline{H}_3$), 0.88 (6H, d., J=5.1cps, $-CH(C\underline{H}_3)_2$), 1.64 (3H, broad s., $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), 5.5 (1H, broad s., $\underline{H}\overset{|}{C}=\overset{|}{C}-$), M^+ion m/e 206 and base peak m/e 121).

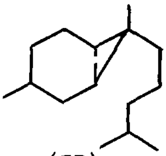
The position of the cyclopropane ring of I is inferred to be at C-1-6-7 by examining the mass spectra of I and its hydrogenated compounds, i.e., the compounds I, II and IV show the base peaks formed by elimination of the chain of six carbon units, whereas, bisabolane (III) shows the most abundant ion formed by losing eight carbon units from molecular ion. This was further confirmed as follows; by dehydrogenation with palladised charcoal, the tetrahydro derivative (II) gave two compounds, namely, dihydro <u>ar</u>-curcumene (V) and the <u>m</u>-substituted isomer (VI). The direct dehydrogenation of I under the same condition yielded V and <u>ar</u>-curcumene (VII).

By comparison of the NMR spectra of I and its dihydro derivative (IV), it is found that one of the double bonds of I corresponds to an isopropylidene group in the side chain and the other should be located at C-2 or C-3. On hydroboration followed by oxidation with chromium trioxide in pyridin, IV gave a ketone (VIII), which shows $\nu_{C=O}$ 1680cm^{-1} and λ_{max} 214mμ (ε 3,150) consistent with six membered cyclic ketone conjugated with cyclopropane ring. Therefore, the position of the carbonyl group, and accordingly the double bond, is decided to be at C-2.

This hydrocarbon undergoes an interesting thermal isomerization when injected into GLC (20%-Carbowax 20M on chromosorb W) at about 200°, yielding a new sesquiterpene hydrocarbon (IX) which has been isolated from the same oil and called β_2-bisabolene by us, ($[\alpha]_D^{25}$ -154.8° (c, 0.31), ν_{max}^{liq} 3080, 1640, 895 and 730cm^{-1}, $\lambda_{max}^{n\text{-}hexane}$ 206.5mμ (ε 7,800), $\delta_{ppm}^{CCl_4}$ 0.96 (3H, d., J=7.2cps, $-\overset{|}{C}H-C\underline{H}_3$), 1.60 and 1.67 (each 3H, broad s., $-\overset{|}{C}=C(C\underline{H}_3)_2$), 4.71 (2H, broad s., $-\overset{|}{C}=C\underline{H}_2$), 5.06 (1H, unresolved m., $\underline{H}\overset{|}{C}=\overset{|}{C}-$) and 5.48 (2H, s., -HC=CH-)). The dihydro derivative (IV) was isomerized under the same condition much easier into the compound (X) (ν_{max}^{liq} 3070, 1635, 890 and 730cm^{-1}, $\delta_{ppm}^{CCl_4}$ 0.87 (6H, d., J=5.7cps, $-CH(C\underline{H}_3)_2$), 0.96 (3H, d., J=6.3cps, $-\overset{|}{C}H-C\underline{H}_3$), 4.74 (2H, broad s., $-\overset{|}{C}=C\underline{H}_2$) and 5.51 (2H, s., -HC=CH-)).



(I)



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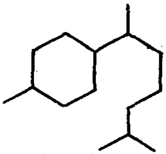

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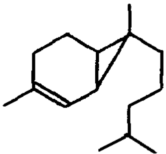

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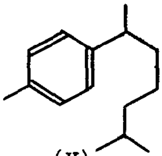
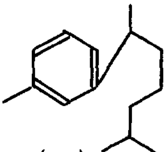
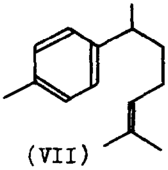


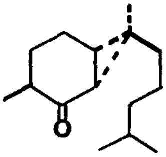
(V)



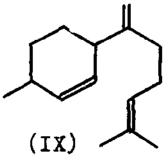
(VI)



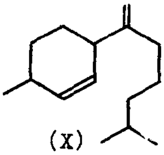
(VII)



(VIII)



(IX)



(X)

(XI)

(XII)

Stereochemistry

The compound (I) is presumed to have the same absolute configuration with (-)-2-carene as shown by the formula (I), because I and its tetrahydro derivative (II) show closely related but opposite $[\alpha]_D$ values, -76.9° and +19.8°, respectively, to those of (+)-2-carene (XI) and (-)-<u>cis</u>-carane (XII), +76.36° and -17.8°, respectively (1). The methyl group attached to the cyclopropane ring was concluded to have an orientation inclining to the cyclohexane ring, as the tertiary methyl group of the ketone (VIII) showed almost the same chemical shift with that of 8-methyl group of 2-caranone (1.15 and 1.17ppm in carbon tetrachloride solution, respectively) (1), and, further, this signal shifted to 1.00ppm on passing from CCl_4 to benzene solution*.

On the other hand, the ketone (VIII) shows positive Cotton effects at 287

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* Such a shielding solvent effect is expected when the methyl group on cyclopropane ring lies <u>quasi</u>-axial to the cyclohexanone ring like an axial methyl group adjacent to a carbonyl group of cyclohexanone, (N.S. Bhacca and D.H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day Inc., San Francisco, Calif., 1964, p 158.).

and 217mμ in its CD curve and the sign of the one at higher wave length does not agree with the above steric structure (CD (c, 0.238 in MeOH) $[\theta]_{323}$ 0, $[\theta]_{287}$ +7250, $[\theta]_{247}$ +850, $[\theta]_{217}$ +10000, $[\theta]_{205}$ +6900). However, it was recently recognized that the optical rotatory dispersion curves of ketones conjugated with cyclopropane ring show two Cotton effects of opposite signs to each other at ca. 300mμ and ca. 210mμ, and one of which at lower wave length is thought to be more reliable for stereochemical problems, as several exceptions have been found in application of the reversed octant rule for the n→π* Cotton effect (2). Thus, the fact that the CD curve of the ketone (VIII) shows a positive Cotton effect at 287mμ means that the reversed contribution of the cyclopropane ring to the n→π* Cotton effect (negative) being overcome by the other substituents.

REFERENCES

1), S. P. Acharya and H. C. Brown, J. Am. Chem. Soc., **89**, 1925 (1967).

2), Private communication from Dr. K. Kuriyama, Shionogi Research Laboratory, and Dr. S. Ito, Tohoku University. We are grateful to them for this information prior ro publication.