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# THE STRUCTURE OF TWO NEW ACETYLENIC NOR-SESQUITERPENOID, DEHYDROCHAMAECYNENOL AND DEHYDROCHAMAECYNENAL, ISOLATED FROM CHAMAECYPARIS FORMOSENSIS MATSUM.

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During the course of a reinvestigation of the terpenoid constituents of Benihi tree (Chamaecyparis formosensis Matsum. Cupressaceae), Nozoe, Cheng and Toda (1) have isolated a novel nor-sesquiterpenoid, chamaecynone and its related natural products which are the first examples of acetylenic compounds of terpenoid origin together with freelingyne reported by Massey-Westropp et al. (2) at about the same time. The structure of chamaecynone was also supported by the total synthesis (3).

Our continuous investigation of the terpenoid fraction of the same tree provided further two new nor-sesquiterpenes, an alcohol and an aldehyde, as minor constituents, whose structural elucidation are described in this paper (4).

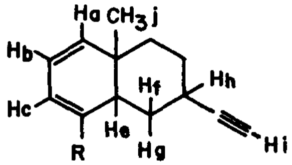
The alcohol named dehydrochamaecynenol (I), $C_{14}H_{18}O$ ($M^+$, 202), colorless oil, $[\alpha]_D^{28.4}$ -193.1° (C = 0.719 MeOH), and the aldehyde named dehydrochamaecynenal (II), $C_{14}H_{16}O$ ($M^+$, 200), colorless oil, were isolated from the fraction of b.p. 113~6°C/1.8 mm of the essential oil of the Benihi tree by column chromatography on silicic acid. The pure alcohol (I) is quite unstable on standing to afford amorphous solid, but gave a stable crystalline 4-bromo-3-nitrobenzoate, m.p. 97°C. The aldehyde (II) is also unstable, and could not be isolated in pure state because of its unstability and the limited amount of the sample.

The UV absorption of I, $\lambda_{max}^{MeOH}$ 264 mμ (log ε 3.55), and II, $\lambda_{max}^{MeOH}$ 305 mμ (log ε 3.74), indicate the presence of homoannular conjugated diene and dienone respectively (5). The IR (neat) of I shows the absorption bands at 3390, 1052 ($-CH_2OH$), 3329, 2119 (-C≡CH), 3012, 1669, 1650, 730 $cm^{-1}$ (cis -CH=CH-), and the IR (neat) of II shows the bands at 2732, 1675 (-CHO), 3322, 2123 (-C≡CH), 741 $cm^{-1}$.

The alcohol (I) and the aldehyde (II) were correlated each other by the following chemical transformation; the reduction of II with $LiAlH_4$ gave I and the oxidation of I with active $MnO_2$ afforded II.

The presence of terminal acetylene group was also confirmed by catalytic hydrogenation of I in the presence of Lindlar catalyst, by which dihydrodehydrochamaecynenol (III), $C_{14}H_{20}O$ ($M^+$, 204), colorless oil, UV; $\lambda_{max}^{MeOH}$ 265 mμ (log ε 3.66), IR; 3356, 1046 ($-CH_2OH$), 3030, 1667, 1645, 995, 910, 729 $cm^{-1}$ ($-CH{=}CH-$ and $-CH{=}CH_2$) was obtained. Further catalytic hydrogenation of III in the presence of Adam's catalyst consumed about three molar equivalents of hydrogen affording saturated octahydro derivative as an oil, $C_{14}H_{26}O$ ($M^+$, 210), therefore, the alcohol (I) is found to be bicyclic.

On the bases of the above spectral data of the compounds I~III, and of chamaecynone (1), together with the known occurence of chamaecynone and the related natural product from the same tree, it is reasonable that the gross structures of I and II can be drawn as shown in Fig. 1.



I R = $CHd_2OH$

II R = CHO

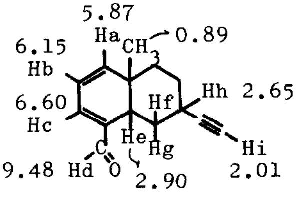
Fig. 1

The NMR spectra (100 Mc) of I were assigned with the aid of decoupling experiments. The NMR of I in pyridine-$d_5$ shows three olefinic protons adjacent each other between 5.4~6.3 ppm and two methylene protons due to allylically located primary alcohol at 4.36 ppm. These three olefinic protons are assigned to Ha, Hb and Hc with following chemical shifts and coupling constants, thus, Ja; 5.38 (d,d,d and unsplit coupling), Hb; 6.02 (d,d), Hc; 6.17 ppm (d,d,t); Jab=8.2, Jac=1.0, Jae=1.2, Jad=0.5, Jbc=5.2 and Jcd=1.5 cps. The values of Jab and Jbc are considered to be reasonable for vicinal coupling through C=C and C-C bond respectively (6).

Some signals appeared upfield from around 3.0 ppm in the NMR of I in $CDCl_3$ could be assigned as follows, He; 2.15 (d,d,d), Hh; 2.71 (m), Hi; 2.03 (d), Hj; 0.91 ppm (3H, s); Jef=4.1, Jeg=12.0 and Jhi=2.5 cps.

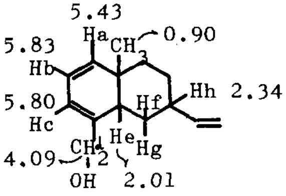
The NMR signals of II (in $CCl_4$, 60 Mc) and III (in $CDCl_3$, 100 Mc) were also assigned as shown in Fig. 2 (ppm unit).

There are twelve possible stereoisomers for I as shown in Fig. 3, i.e., A,B; trans, C, D; cis-fused steroid conformation, E, F; cis-fused non-steroid conformation, and their mirror images (A'~F').



II

Jab=10.0cps
Jac=1.5
Jae=1.5
Jbc=5.0
Jeg=13.0
Jef=5.0
Jhi=2.5



III

Jab=8.3cps
Jac=1.2
Jad=~0.5
Jae=1.1
Jef=5.2
Jeg=10.2

Fig. 2

I $R_1$ = $CH_2OH$
$R_2$ = $C\equiv CH$
II $R_1$ = CHO
$R_2$ = $C\equiv CH$

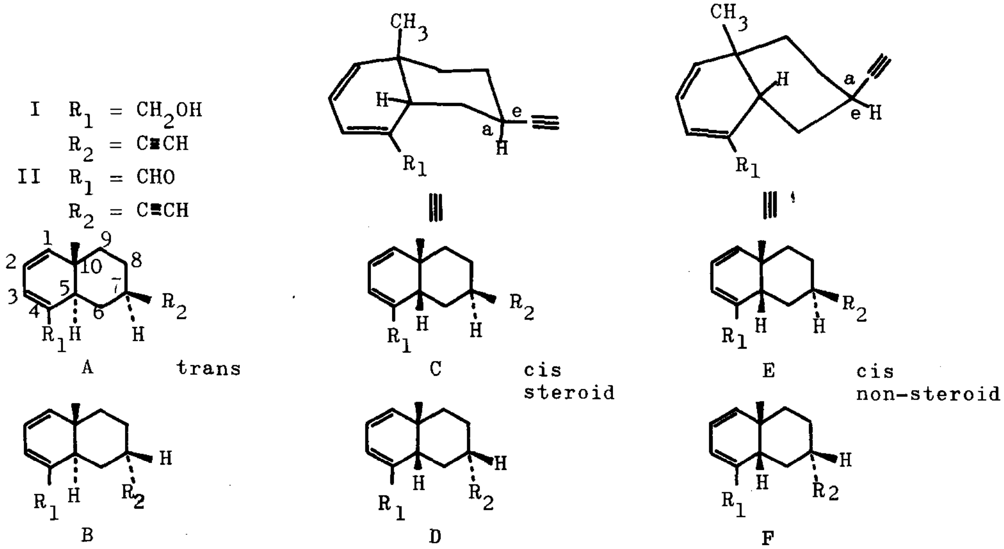
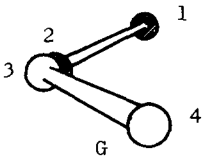
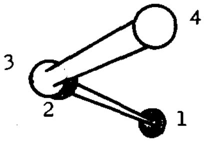


Fig. 3

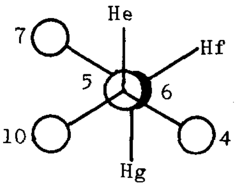
The ORD curve of I showed a strong negative Cotton effect ($[\Phi]_{281}$ -13,300, $[\Phi]_{225}$ + 28,800 A = -421 in MeOH) indicates that the cisoid diene chromophore must be twisted in the sence of a righthanded helix (G) according to helicity rule (7). The compound III also showed a negative Cotton effect ($[\Phi]_{288}$ -23,900, $[\Phi]_{233}$ + 37,100 A = -610 in MeOH) in its ORD curve. This ruled out the formulae C, D, A', B', E' and F', in which the diene chromophore twisted in a lefthanded helix (H).



G



H



J

In the NMR of I, the facts that Jae is 1.2 cps and no splitting is observed between Hc and He indicate (8) the fragment Ha-$C_1$-$C_{10}$-$C_5$-He would be in the zigzag coplaner relationship and the fragment Hc-$C_3$-$C_4$ —$C_5$-He is in coplaner relationship respectively. This conclusion excludes the posibility of the formulae A~D and their mirror images A'~D' by the examination of Dreiding models. The formulae C, D and C', D' are also excluded from a consideration of the magnitudes of Jef=4.1 and Jeg=12.0 which indicate the conformation around $C_5$ and $C_6$ can be shown as J.

Remarkable down field shift of He proton in the NMR of II due to aldehyde carbonyl group shows the fragment He-$C_5$-$C_4$-C=O must be coplaner relationship. This fact together with ORD curve of II showed a negative Cotton effect ($[\Phi]_{318}$ -6,820, $[\Phi]_{250}$ + 8,230) also indicates that the conformation of I and II are cis-fused non-steroid form (E or F).

To determine the structure of I and II from the remaining two possible formulae E and F which have α- (axial) and β- (equatorial) orientated acetylene group respectively, half-band widths of hydrogens Hh were examined.

The half-band widths of Hh in the NMR of I, II and III are so small as 11, 12 and 14 cps respectively. These values ruled out the formula F because axial Hh in F would show much larger value by coupling with vicinal two axial and two equatorial hydrogens. Therefore, the formula E, possessing novel non-steroid cis-fused hydronaphthalene with axial terminal acetylene group, was proposed for I and II including the absolute configuration.

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