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NEW SESQUITERPENOIDS FROM SCHISANDRA CHINENSIS

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A sesquiterpene hydrocarbon, β-chamigrene (I), was isolated for the first time from the leaf oil of Chamaecyparis taiwanensis by Itō and his colleagues (1) (2). Recently, we isolated the same hydrocarbon from the oil of the fruits of Schisandra chinensis together with two new compounds of the same carbon skeleton, namely, α-chamigrene and chamigrenal.

α-Chamigrene (II), $C_{15}H_{24}$, $[\alpha]_D$ -14.5° (c, 0.21 in chloroform), was isolated from the hydrocarbon fraction of the oil by the same way reported in a previous paper (6). Its i.r. spectrum shows bands at 1655, 830, 810, 800 and 760cm^{-1}. Mass spectrum of II showed molecular ion at m/e 204 and characteristic ions at m/e 136 (r.i. 100%) and m/e 121 (r.i. 91%). The n.m.r. spectrum exhibited signals of two trisubstituted double bonds, δ^{CCl4}_{ppm} 1.63 (6H, broad s.) and 5.3 (2H, unresolved m.), along with two quaternary methyl groups, 0.84 and 0.89 (each 3H, s.).

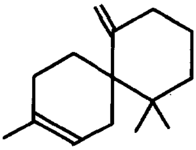
On hydrogenation in acetic acid using platinum oxide as catalyst, II afforded two tetrahydro derivatives in a ratio of about 2 : 1 and the major one of them was identified as chamigrane by comparison of its i.r. and mass spectra and retention time (Rt) in GLC with those of the authentic sample obtained from β-chamigrene (I) by the same procedure. The minor component showed the identical mass spectral pattern but different i.r. spectrum and Rt in GLC with those of the authentic chamigrane, and it was considered to be an isomer having a different orientation of the methyl group at C-9. Thus, the carbon skeleton of II was concluded to be chamigrane and the two trisubstituted double bonds carrying methyl substituent were located unequivocally at C-1 and C-8 as shown in the formula (II) (3) (4).

This hydrocarbon was identical in all respects with the one obtained by Yoshikoshi and his colleagues as a by-product in the course of synthetic preparation of β-chamigrene (5).

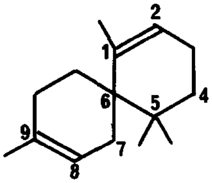
Chamigrenal (III), $C_{15}H_{22}O$, $[\alpha]_D$ -80.5° (c, 0.60 in chloroform), was isolated from the oxygenated compound fraction of the oil by chromatography over silica gel column followed by gas chromatographic separation. Its i.r. spectrum shows absorption bands at 3080, 2700, 1685, 1640, 890 and 780cm^{-1}. The n.m.r. spectrum (in CCl_4) exhibited following signals: two tertiary methyl singlets (at 0.87 and 0.90ppm), a pair of one proton singlets of terminal methylene grouping (centered at 4.34 and 4.84ppm), a vinyl proton multiplet (centered at 6.73 ppm) and a singlet of aldehyde proton (at 9.30ppm). These data and a characteristic maximum at 231mμ (ε, 12,160) in its UV spectrum indicate the presence of α,β-unsaturated aldehyde group in the molecule.

The Wolff-Kishner reduction of the semicarbazone of III yielded two hydrocarbons, I and IV, in a ratio of 2.4 : 1 and the major one of them was identified as β-chamigrene (I) by comparison of its i.r. and mass spectra and Rt in GLC with those of the authentic sample. The minor product was shown to have two terminal methylene groups by i.r. and n.m.r. spectra [ν_{max} 3070, 1640 (sh.), 1630, 900 and 890cm^{-1}, $\delta_{ppm}^{CCl_4}$ 0.85 (6H, s. $-\overset{|}{C}(C\underline{H}_3)_2$), 4.46 (2H, $-\overset{|}{C}=C\underline{H}_2$), 4.73 and 5.09 (each 1H, $-\overset{|}{C}=C\underline{H}_2$)], and considering from the nature of the reaction, it was concluded to have a structure shown by the formula (IV), which was named γ-chamigrene by us. Accordingly, the carbon skeleton of III was decided to be chamigrane and the position of the aldehyde group was concluded to be at C-9 as shown in the formula (III).

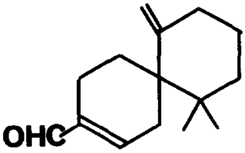
By the way, a primary alcohol named chamigrenol (V) was obtained by reducing the aldehyde (III) with lithium aluminum hydride and its structure was consistent with its i.r., mass and n.m.r. spectra: ν_{max} 3300, 1625 and 890cm^{-1}, M^+ion m/e 220, $\delta_{ppm}^{CCl_4}$ 0.83 and 0.88 (each 3H, s. $-\overset{|}{C}(C\underline{H}_3)_2$), 2.74 (1H, s. $-O\underline{H}$), 3.87 (2H, broad s. $-C\underline{H}_2OH$), 4.49 and 4.88 (each 1H, $-\overset{|}{C}=C\underline{H}_2$) and 5.6 (1H, m. $-\overset{|}{C}=\overset{|}{C}\underline{H}$).



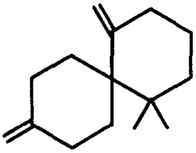
I



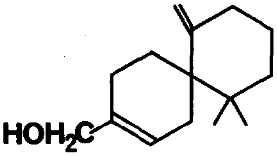
II



III



IV

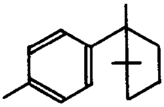


V

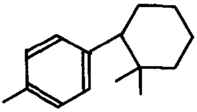
1), S. Itô, K. Endo, T. Yoshida, M. Yatagai and M. Kodama, Chem. Commn., 1967, 186.

2), Dr. S. Itô agreeded with our proposal to call the chamigrene (I) isolated from C. taiwanensis as β-chamigrene to avoid confusions.

3), α-Chamigrene may be a thermal isomerization product of β-isomer, as, on dehydrogenation of β-chamigrene with palladised charcoal, a considerable amount of α-isomer was formed together with cuparene (VI) and isocuparene (VII) (tentatively named).

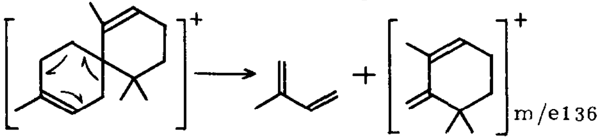


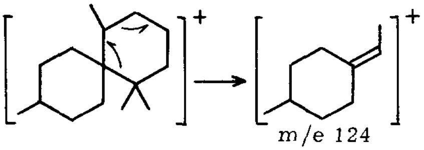
VI



VII

4), The mass spectra of β- and α-chamigrene and chamigrane showed extremely characteristic patterns in which the base peak ions appeared at m/e 189 (M-15), m/e 136, and m/e 124, respectively. The easiness of the elimination of a methyl group from the molecular β-chamigrene ion is interpreted as invoked by the steric hindrance supposed to exist between the methyl group at C-5 and the terminal methylene group, and this phenomenon is consistent with the fact that the trisubstituted double bond of β-chamigrene was selectively hydrogenated (1). The mechanisms of the formation of base peak ions of other two compounds were interpreted by the following schemes.





5), A. Tanaka, H. Uda and A. Yoshikoshi, Abstractbook of the Symposium on the Chemistry of Terpenes, Essential Oils and Aromatics in 1967, p.77.

6), Y. Ohta and Y. Hirose, to be published in Tetrahedron Letters, No.10, 1968.