

Chamigrene, a Sesquiterpene Hydrocarbon of a Novel Carbon Skeleton

By SHÔ ITÔ, KATSUYA ENDO, TSUNEMASA YOSHIDA, MITSUYOSHI YATAGAI, and MITSUAKI KODAMA

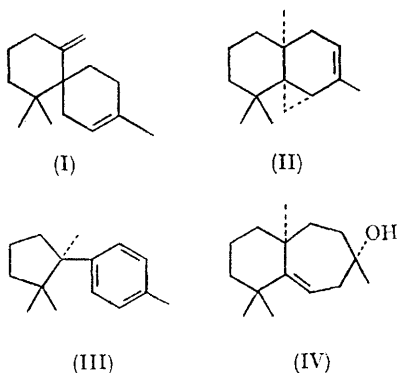
(Department of Chemistry, Tohoku University, Sendai, Japan)

THROUGH an extensive separation¹ of the neutral essential oil from the leaves of *Chamaecyparis taiwanensis* Masam., we have isolated a new sesquiterpenic hydrocarbon and now present evidence which permits us to assign the structure

(I)—a unique spiro-ring system—to this hydrocarbon.

A combination of alumina and silica gel (AgNO₃ impregnated) chromatography of the sesquiterpenic part of the neutral essential oil afforded

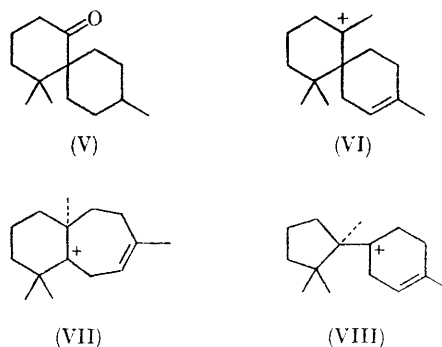
chamigreene (I) in 3% yield based on the neutral essential oil, in addition to 17 known compounds¹ including thujopsene² (II), α - and β -cedrenes, cuparene³ (III), cedrol, widdrol⁴ (IV), thujopsenal⁵ and mayurone.⁶ Compound (I) is a colourless oil, $C_{15}H_{24}$, M^+ 204, b.p. 110–113°/13 mm. Hg, n_D^{22} 1.5062, $[\alpha]_D^{15}$ -52.7° ($CHCl_3$), R_t 1.28.* The i.r. spectrum (liquid) showed absorptions at 1638 and 890 cm^{-1} ($>C=CH_2$) and 800–820 cm^{-1} ($CH=C<$) as well as twin bands at 1368 and 1388 cm^{-1} (Me_2C), while the n.m.r. spectrum (60 Mc./sec. in CCl_4) displayed two methyl signals (singlets at 0.82 and 0.87 p.p.m.), allylic methyl signal at 1.55 p.p.m. weakly coupled with a multiplet at 5.22 p.p.m. due to a vinylic proton on a trisubstituted double bond, and two vinylidene proton signals, at 4.47 (1H; $J = 2$ c./sec.) and 4.82 p.p.m. (1H; $J = 2$ and 1 c./sec.).



The same hydrocarbon (I) was isolated as one of the major products from the hydrocarbon mixture obtained either by the isomerization of thujopsene (II) with oxalic acid⁷ or by the acid-catalyzed dehydration of widdrol (IV),⁸ thus disclosing the close structural relationship between chamigreene, thujopsene, and widdrol.

The vinylidene group in chamigreene is sterically hindered compared with the other double bond, since osmium tetroxide oxidation of (I) afforded in good yield an unsaturated diol,† $C_{15}H_{26}O_2$, m.p. 93–94°, $[\alpha]_D -11^\circ$ (methanol), which still contained the vinylidene group [$\nu_{max}(KBr)$ 895 cm^{-1} , $\delta(CCl_4)$ 4.63, 5.00 p.p.m. (both broad singlet)]

and two methyl groups (δ 0.89 p.p.m.) originally present in (I), but which lacked the trisubstituted double bond (no corresponding absorption in i.r. and n.m.r. spectra). The presence of a 1,2-glycol system in the diol was detected by i.r. (ν 3400, 1020 cm^{-1}) and n.m.r. [$\delta(CCl_4)$ 3.20–3.50 (1H; multiplet, $CH_2\cdot CH\cdot OH$) and 1.11 (singlet, $CH_3\cdot C\cdot OH$)] and confirmed by the formation of an oily acetone, $C_{15}H_{28}O_2$, ν_{max} (liquid) 1635, 1060, 890 cm^{-1} (no OH band), δ 0.85, 0.87, 1.18, 1.31, 1.38 (all 3H singlets), 4.00 (1H, triplet, $J = 7.5$), 4.60 (1H; doublet, $J = 2$), 4.86 (1H, broad singlet). The sterically hindered nature of the vinylidene group in chamigreene was also shown from the catalytic hydrogenation (palladium-charcoal) which afforded a mixture of dihydro- (R_t 1.26) and tetrahydro-chamigreene (R_t 1.05). Ozonolysis of the mixture and oxidative decomposition of the ozonide followed by alumina chromatography afforded the liquid nor-ketone (V), $C_{14}H_{24}O$, as well as pure tetrahydrochamigreene, $C_{15}H_{28}$, M^+ 208. The i.r. spectrum (liquid) of the nor-ketone clearly exhibited a strong band at 1711 cm^{-1} indicating the presence of a carbonyl group in a six-membered or larger ring. However, this ketone displayed only a plain o.r.d. curve (in methanol, $[\Phi]_{300} +10^\circ$, $[\Phi]_{280} +30^\circ$, $[\Phi]_{260} +60^\circ$) revealing the absence of any asymmetric centre at least in the vicinity of the carbonyl group. The above experimental evidence is only compatible with structure (I) for chamigreene.‡ To our knowledge, this is the first instance of a spiro[5,5]undecane system being found in a sesquiterpenoid.



The occurrence of (I) in Nature is significant since it corresponds to a probable link (VI) in the

* Satisfactory analytical values were obtained for the compounds described. Retention times (R_t) in gas chromatography are expressed relative to that of thujopsene. Chemical shifts are in p.p.m. downfield from Me_4Si .

† This diol could be a mixture of diastereoisomers, but no experimental indication of this was obtained.

‡ For the synthesis of this hydrocarbon, see the following Communication by A. Tanaka, H. Uda, and A. Yoshikoshi.

biogenesis of both thujopsene (through the ion VII)¹ and the cuprenenes and cuparene (through the

ion VIII),⁹ although the exact biogenetic sequence is still unknown.

(Received, January 2nd, 1967; Com. 003.)

¹ T. Yoshida, K. Endo, S. Itô, and T. Nozoe, *J. Pharm. Soc. (Japan)*, 1967, **87**, in the press.

² T. Norin, *Acta Chem. Scand.*, 1963, **17**, 738 and Papers cited therein.

³ C. Enzell and H. Erdtman, *Tetrahedron*, 1958, **4**, 361.

⁴ S. Itô, K. Endo, and T. Nozoe, *Tetrahedron Letters*, 1965, 3375 and Papers cited therein.

⁵ H. Erdtman and T. Norin, *Acta Chem. Scand.*, 1959, **13**, 1124.

⁶ G. L. Chetty and S. Dev, *Tetrahedron Letters*, 1965, 3773; S. Itô, K. Endo, H. Honma, and K. Ota, *ibid.*, p. 3777.

⁷ S. Nagahama, *Bull. Chem. Soc. Japan*, 1960, **33**, 1467. W. G. Dauben and L. F. Friedrich, *Tetrahedron Letters*, 1964, 2675.

⁸ K. Endo, M. Kodama, M. Yatagai, and S. Itô, to be published.

⁹ W. G. Dauben and P. Oberhänsli, *J. Org. Chem.*, 1966, **31**, 315.