Communications to the Editor

[Chem. Pharm. Bull. 27(1) 274—275 (1979)]

UDC 547.594.4.04 : 547.562.1.04

A New Synthesis of α-Chamigrene

α-Chamigrene has been synthesised *via* a new spiro-annelation reaction, copper(II) chloride catalysed decomposition of phenolic α-diazoketone (III).

Keywords——total synthesis; α-chamigrene; spiro[5.5]undecane; spiro-annelation; reaction; phenolic α-diazoketone

In a previous paper,[1] we described a new synthetic method of spiro[4.5]decane carbon framework *via* metal catalysed decomposition of phenolic α-diazoketones. Now we extend this reaction to the synthesis of α-chamigrene (I).[2]

4-Methyl-4-(*p*-hydroxyphenyl)pentanoic acid[3] was protected at the phenolic hydroxy group by acetylation (Ac_2O, aqueous NaOH) and then converted to the acyl chloride (II) ($SOCl_2$, benzene). Slow addition of II to an ethereal solution of diazoethane[4] at 0°, followed by hydrolysis (Na_2CO_3, $NaHCO_3$, aqueous methanol)[5] gave the phenolic α-diazoketone (III) in over all 70% yield. Decomposition of III in the presence of cupric chloride on refluxing benzene gave the spiro-dienone (IV)[6] (20%), mp 143—144°, infrared spectrum (IR) $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1660, and 1620; ultraviolet spectrum (UV) λ_{max}^{EtOH} nm (ε): 241 (1.7×10^4). Partial reduction of IV with sodium borohydride in methanol at 0° gave with stereoselectivity (the *trans*-alcohol, <5%) the *cis*-alcohol (V) (80%), mp 193—194°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 and 1620; UV λ_{max}^{EtOH} nm (ε): 248 (1.5×10^4); proton magnetic resonance (PMR) δ ($CDCl_3$): 4.00 (1H, m, *W* 1/2=8 Hz, -ĊH-O-). The spiro-dienone (V) was catalytically hydrogenated (H_2/Pd-C, AcOEt) to give the saturated ketone (VI) (90%), mp 96—97°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, and which was converted to the spiro-undecene (VIII)[2d] [50% from (VI)], mp 52—53°, by warming the corresponding mesylate (VII) (MsCl, pyridine) in dimethyl sulfoxide at 60°. The ketone (VIII) was treated with methylmagnesium iodide to give a mixture of diastereomeric alcohols (IX) (80%). Without separation, the mixture of alcohol underwent dehydration (silica gel-$FeCl_3$)[7] to give α-

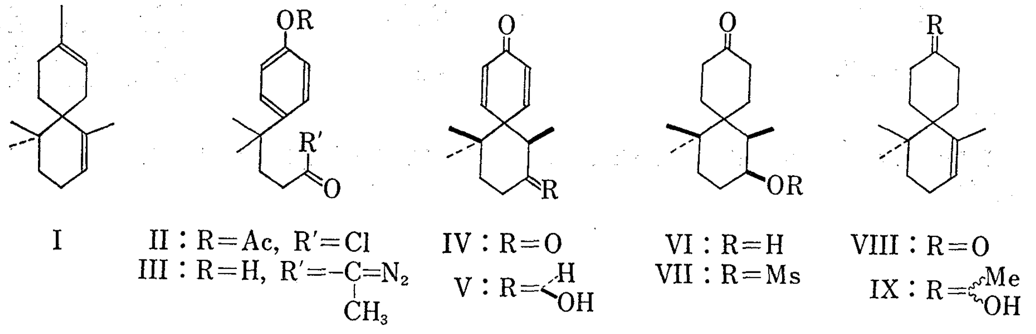

Chart 1

---

[1] C. Iwata, M. Yamada, Y. Shinoo, K. Kobayashi, and H. Okada, *Chem. Commun.*, **1977**, 888.

[2] *a*) S. Kanoo, *Chem. Commun.*, **1967**, 1257; *b*) A. Tanaka, H. Uda, and A. Yoshikoshi, *Chem. Commun.*, **1968**, 56; *c*) Y. Ohta and Y. Hirose, *Tetrahedron Lett.*, **1968**, 2483; *d*) J. D. White, S. Torii, and J. Nogami, *Tetrahedron Lett.*, **1974**, 2882; *e*) G. Frater, *Helv. Chim. Acta*, **60**, 515 (1977).

[3] D.I. Schuster and W.V. Curran, *J. Org. Chem.*, **35**, 4192 (1970).

[4] J.A. Marshall and J.J. Partrige, *J. Org. Chem.*, **33**, 4090 (1968).

[5] D.J. Beames and L.N. Mander, *Aust. J. Chem.*, **27**, 1257 (1974).

[6] Satisfactory analytical and spectral data were obtained for new compounds.

[7] E. Krinan and Y. Mazur, *J. Org. Chem.*, **43**, 1020 (1978).

chamigrene (I). This product was identified by spectral comparison with an authentic α-chamigrene.

Acknowledgement We thank Professor S. Torii of Okayama University for kindly providing IR and PMR spectra of α-chamigrene.

Faculty of Pharmaceutical Sciences
Osaka University
133-1, Yamadakami, Suita, Osaka
565, Japan

CHUZO IWATA
MINORU YAMADA
YASUTAKA SHINOO

Received October 9, 1978

[Chem. Pharm. Bull. 27(1) 275—278 (1979)]

UDC 547.913.2.02 : 581.192

Two New Sesquiterpenoids from *Asarum caulescens*

Two new sesquiterpenoids, caulolactone A(II) and caulolactone B(III) were isolated from *Asarum caulescens.* It was suggested that they were formed via the conformers I-A and I-B of germacrone-4,5-epoxide (I) respectively. Moreover, two configurational isomers of germacrone-1,10; 4,5-diepoxides (IV and V) were derived from I also *via* I-A and I-B.

Keywords——sesquiterpenoids; caulolactone A; caulolactone B; transannular rearrengement; *Asarum caulescens*; germacrone-1,10; 4,5-diepoxide

Previously, the authors have reported the structures of 12 new sesquiterpenoids from essential oil contained in *Asarum caulescens* MAXIM. (Aristolochiaceae) collected at various parts of Japan.[1]

In this report, the authors wish to report the structures of the two new sesquiterpenoids named as caulolactone A (II) and caulolactone B(III), in addition to main component, germacrone-4,5-epoxide (I)[1a] from *Asarum caulescens* collected at Mt. Khotsu in Tokushima Prefecture. The subterranean part of the plant were extracted with ether at room temperature. The extract was chromatographed on silica gel by using petroleum ether–diethylether (5: 1) to give I (48%), II (1.2%), and III (1.0%). Compounds II and III were also derived from I by treating with anhydrous aluminium chloride in absolute ether, of yields 10% and 8%, respectively (Chart 2).

Caulclactone A(II): Colorless needles, mp 97—98°, $C_{15}H_{22}O_2$ $[\alpha]^{25}_{D}=+170°$ (c, 0.3, MeOH), IR $\nu^{CCl_4}_{max}$ 1715 cm^{-1}, UV λ^{MeOH}_{max} 234 nm (ε, 16000). These data showed the presence of α,β-unsaturated lactone group in the molecule, and also CD ($[\theta]_{235}+700$, $[\theta]_{210}+840$) supported the presence of this group.[2] ^{1}H-NMR (δCCl_4+TMS) 1.18 (*tert.* methyl on a carbon atom bounded with an oxygenic function), 1.72, 1.81, 2.13 (three olefinic methyls), 4.74 (2H, s, terminal methylene).

II was heated with 10% HCl/aq. methanol to give three compounds: VI being shifted the double bond from terminal to isopropylidene type, mp 105—106°, $C_{15}H_{22}O_2$, $\nu^{CCl_4}_{max}$ 1715 cm^{-1}, λ^{MeOH}_{max} 234 nm (ε, 1600), $\delta^{CCl_4}_{ppm}$ 1.22 (*tert.* methyl), 1.55, 1.58 (isopropylidene), 1.74, 2.18

---

[1] *a*) J. Endo and M. Nagasawa, *Yakugaku Zasshi*, **94**, 1574 (1974); *b*) J. Endo, *ibid.*, **97**, 393 (1977); *c*) J. Endo, T. Nakamura, and M. Nagasawa, *Shokubutsu Kenkyu Zasshi*, **51**, 209 (1976).

[2] R. Toubiana, M.-J. Toubiana, K. Tori, and K. Kuriyama, *Tetrahedron Lett.*, **1974**, 1753.