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

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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°, $C_{15}H_{22}O_2$ $[\alpha]_D^{25}=+170°$ (*c*, 0.3, MeOH), IR $\nu_{max}^{CCl_4}$ 1715 cm^{-1}, UV λ_{max}^{MeOH} 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°, $C_{15}H_{22}O_2$, $\nu_{max}^{CCl_4}$ 1715 cm^{-1}, λ_{max}^{MeOH} 234 nm (ε, 1600), $\delta_{ppm}^{CCl_4}$ 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.

(isopropylidene); VII being added with a methoxyl group at C-10, oil, $C_{16}H_{26}O_3$, $\nu_{max}^{CCl_4}$ 1710 cm^{-1}, λ_{max}^{MeOH} 234 nm (ε, 16000), $\delta_{ppm}^{CCl_4}$ 1.12 (*tert.* methyl), 1.20, 1.25 $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\times\!\!O-\right)$, 1.84, 2.17 (isopropylidene), 3.17 ($-OCH_3$); VIII having a hydroxyl group at C-10, oil, $C_{15}H_{24}O_3$, $\nu_{max}^{CCl_4}$ 3450, 1710 cm^{-1} λ_{max}^{MeOH} 234 nm (ε, 16000), $\delta_{ppm}^{CCl_4}$ 1.20 (*tert.* methyl), 1.22, 1.23 $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\times\!\!O-\right)$, 1.84, 2.17 (isopropylidene). Further both VII and VIII gave VI under the same condition mentioned above. On the other hand, dihydro derivative IX was prepared from II by catalytic reduction with Pd-C/MeOH. Further, tetrahydro derivative X was also obtained from IX by catalytic reduction with PtO_2/AcOH (Chart 1). IX: $C_{15}H_{24}O_2$, oil, $\nu_{max}^{CCl_4}$ 1710 cm^{-1}, $\lambda_{max}^{CCl_4}$ 234 nm (ε, 16000), $\delta_{ppm}^{CCl_4}$ 0.88, 0.92 (isopropyl, d, J=7.0), 1.13 (*tert.* methyl), 1.79, 2.08 (isopropylidene). X: $C_{15}H_{26}O_2$, oil, $\nu_{max}^{CCl_4}$ 1725 cm^{-1}, $\delta_{ppm}^{CCl_4}$ 0.85—0.97 (2×isopropyl), 1.16 (*tert.* methyl).

Consequently, it was supposed the structure of caulolactone A as II or III from the results mentioned above.

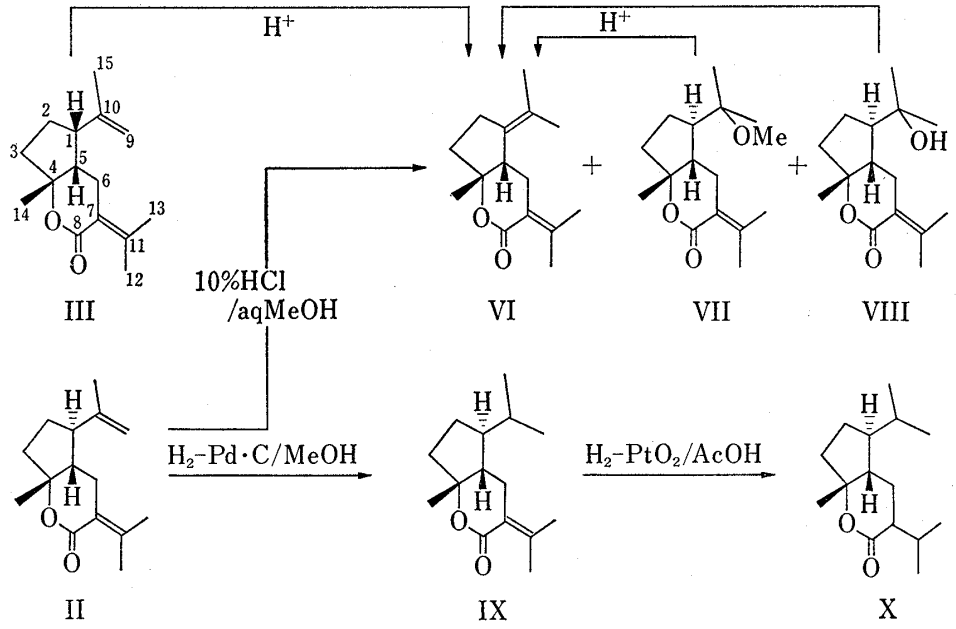


Chart 1

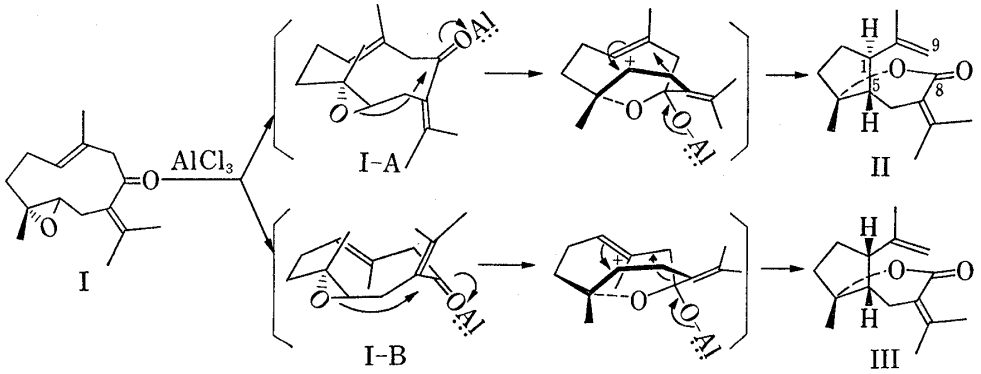


Chart 2

Caulolactone B (III): colorless oil, $C_{15}H_{22}O_2$, $[\alpha]_D^{25}=+8.8°$ (*c*, 0.2, MeOH), $\nu_{max}^{CCl_4}$ 1712 cm^{-1}, λ_{max}^{MeOH} 232 nm (ε, 18000), $[\theta]_{238}+640$, $[\theta]_{228}+680$, $\delta_{ppm}^{CCl_4}$ 1.16 (*tert.* methyl), 1.75, 1.80, 2.10 (three olefinic methyl), 4.78, 4.92 (terminal methylene). Spectral data of this compound was very similar to that of II. III was easily derived to VI by treating with acid as well as II. This result suggested that II and III were the stereoisomers of the isopropenyl group. Configurations at C-1 of both isomers were confirmed by chemical shifts of terminal methylene at C-9 as follows. The chemical shifts (4.74 ppm, 2H, s) indicated equivalent protons at C-9 and was assigned to the structure II for caulolactone A from the less effect by anisotropy of lactone ring. The other non-equivalent protons at C-9 (4.78 and 4.92 each 1H) showed to be assigned to the structure III for caulolactone B. These results suggested that the stereoisomers II and III originated from the possible conformers of I-A and I-B respectively and the proton at C-5 was assumed to be β-configuration, according to reaction mechanism (Chart 2). These two compounds, II and III, are the unique natural products having the skelton fissioned at C8-C9 from ten membered ring.

The presence of these two conformers was supported also from the other reaction. I was treated with *m*-chloroperbenzoic acid to produce the two stereoisomers, 1,10; 4,5-diepoxygermacrone, IV[3] and V (Chart 3). IV; mp 105—106°, $C_{15}H_{22}O_3$, $[\theta]_{250}-22000$, $[\theta]_{324}+5000$, λ_{max}^{MeOH} 249 nm (ε, 4800), ν_{max}^{KBr} 1678 cm^{-1}, $\delta_{ppm}^{CDCl_3}$ 1.15, 1.45 (each s, $>\overset{O-}{\underset{}{C}}\underline{CH_3}-$), 1.81, 1.86 (each s, isopropylidene methyl), 2.62 (1H, dd, J=11, 1 Hz, C5-H), 2.64 (1H, dd, J=11, 2Hz, C1-H). V; mp 131—132°, $C_{15}H_{22}O_3$, $[\theta]_{250}+20000$, $[\theta]_{324}-5000$, λ_{max}^{MeOH} 250 nm (ε, 5200), ν_{max}^{KBr} 1673 cm^{-1}, $\delta_{ppm}^{CDCl_3}$ 1.34, 1.37 (each s, $>\overset{O-}{\underset{}{C}}\underline{CH_3}-$), 1.77, 1.78 (each s, isopropylidene) 2.64 (1H, dd, J=11, 2 Hz, Cl- or C5-H), 2.70 (1H, dd, J=11,1 Hz, C5- or C1-H). IV was decided to have the structure of IV-a by X-ray analysis.[4] Consequently, the other one was suggested to have the structure V of its configurational isomer.

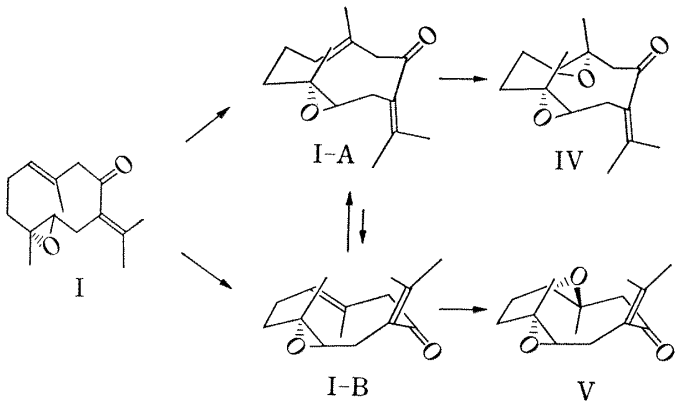
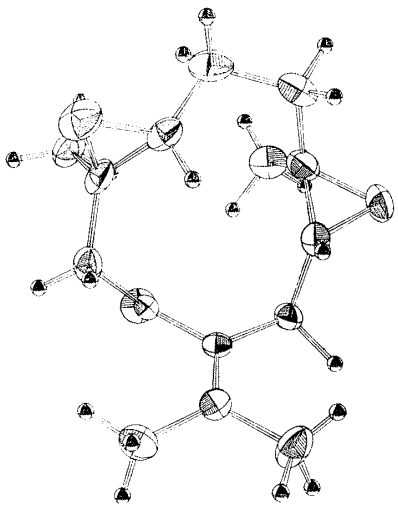


Chart 3



IV-a

The reaction mechanism was proceeded by addition oxygen function to the ring double bond from the outside of ten membered ring. So, it was assumed that I had two conformers I-A and I-B to produce IV and V as same as Chart 2.

3) H. Hikino, C. Konno, T. Nagashima, T. Kohama, and T. Takamoto, *Tetrahedron Lett.*, **1971** 337.
4) Detail data will be reported later.

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