The studies about the mechanism of FAA formation and its biological activity are going on now. The details of this study will be reported near future.

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Arnottinin: Structural Establishment by Chemical Correlation with Osthenol

The structure of arnottinin (**1**) was established by the transformation of osthenol (**2**) to it.

In the previous paper,[1] we reported the isolation of arnottinin (**1**), a new phenolic coumarin from the xylem of *Xanthoxylum arnottianum* Maxim. (Japanese name: Iwa-Zansho). We wish to report here its structural establishment by means of chemical correlation of arnottinin (**1**) with osthenol (**2**).

Arnottinin (**1**) is obtained as colorless needles, mp 191—193°, $C_{14}H_{14}O_4$. It shows the following spectral data. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3290, 3100 (OH), 1693 (C=O); NMR (CD_3OD) δ: 1.74 (3H, s, vinyl CH_3), 3.55 (2H, d, J=7.0 Hz, $ArC\underline{H}_2CH{=}C$), 4.34 (2H, s, $C{=}C(C)C\underline{H}_2OH$), 5.35 (1H, dif. t, J=7.0 Hz, $CH_2C\underline{H}{=}C$), 6.14 (1H, d, J=9.6 Hz, C_3–H), 6.77 (1H, d, J=8.6 Hz, C_6–H), 7.29 (1H, d, J=8.6 Hz, C_5–H), 7.80 (1H, d, J=9.6 Hz, C_4–H); $[\alpha]_D^{20}$ ±0° (c=0.65, EtOH). Inspection of these spectral data with regard to the general biogenetic pathway of coumarins allowed to depict the structure of arnottinin with the structure **1**, its geometrical isomer (**3**), or the structural isomer (**4**). As arnottinin, however, showed no optical rotation we could exclude the structure **4** from the possible structures. Unfortunately, the yield of arnottinin from the plant (*ca* 0.0018%) is so scarce that we could not establish its structure by chemical means. Therefore, we attempted to chemically correlate this coumarin with osthenol (**2**).

In 1973, Steck[2] reported that hydrolysis of macrocarpin (**5**) gave a coumarin (**6**), the structure of which was supposed to correspond to the methyl ether of arnottinin. Therefore, we first aimed at synthesizing this coumarin (**6**) as a model experiment.

In 1972, for allylic oxidation of olefins by SeO_2, Sharpless, *et al.*[3] proposed a mechanism which suggested an initial ene addition[4] of Se^+–O^- moiety followed by dehydration and [2,3]-sigmatropic shift of the resulting allylseleninic acid. This mechanism suggests that oxidation of osthol (**7**) with SeO_2 should give the coumarin (**8**) having an E-configuration, because the ene reaction takes place at the least substituted allylic position preferentially and [2,3]-sigmatropic rearrangement of the resulting allylseleninic acid derivative (**9**) should proceed through the process giving an E-configuration product.

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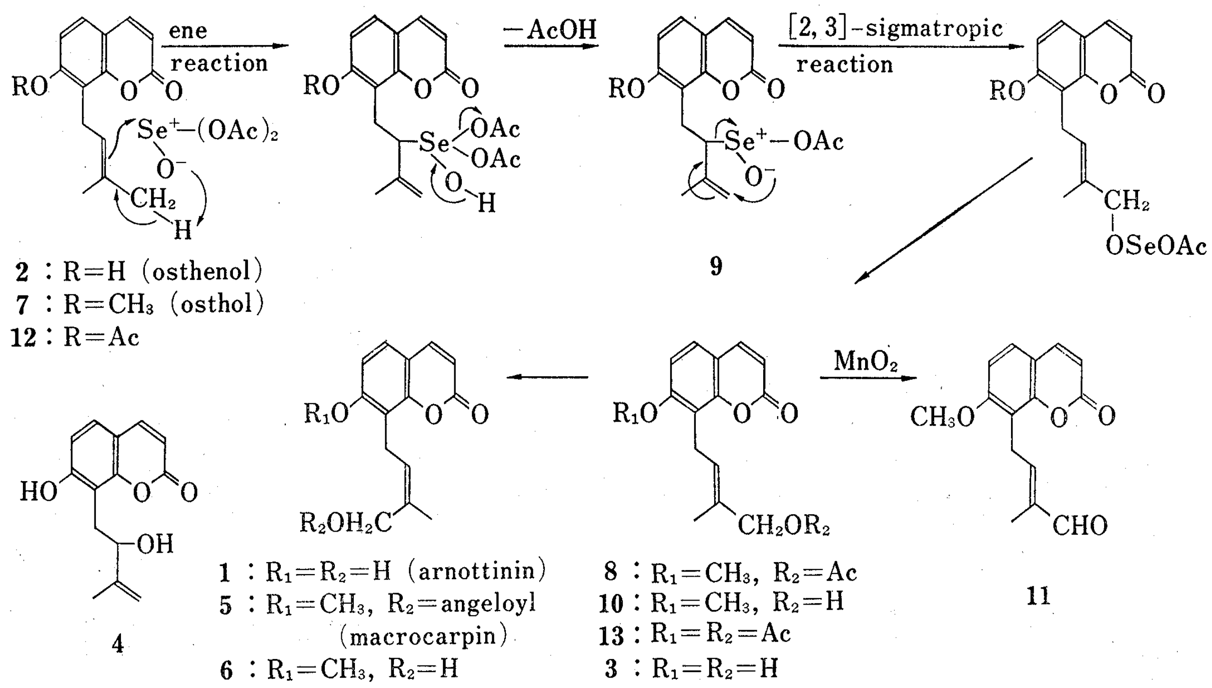
[1] H. Ishii, K. Hosoya, T. Ishikawa, and J. Haginiwa, *Yakugaku Zasshi*, **94**, 309 (1974); H. Ishii, K. Hosoya, T. Ishikawa, E. Ueda, and J. Haginiwa, *ibid.*, **94**, 322 (1974).

[2] W. Steck, *Phytochemistry*, **12**, 2283 (1973).

[3] K.B. Sharpless and R.F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972); D. Arigoni, A. Vasella, K.B. Sharpless, and H.P. Jensen, *ibid.*, **95**, 7917 (1973).

[4] H.M.R. Hoffmann, *Angew. Chem. Intern. Ed. Engl.*, **8**, 556 (1969).



2 : R=H (osthenol)
7 : R=CH_3 (osthol)
12 : R=Ac

4

9

1 : $R_1=R_2=H$ (arnottinin)
5 : $R_1=CH_3$, R_2=angeloyl (macrocarpin)
6 : $R_1=CH_3$, $R_2=H$

8 : $R_1=CH_3$, $R_2=Ac$
10 : $R_1=CH_3$, $R_2=H$
13 : $R_1=R_2=Ac$
3 : $R_1=R_2=H$

11

Chart 1

Treatment of osthol[5] (**7**) with SeO_2 in Ac_2O gave **8** as colorless needles, $C_{17}H_{18}O_5$, mp 100—102°, [NMR ($CDCl_3$) δ: 2.01 (3H, s, $COCH_3$), 3.57 (2H, d, J=7.0 Hz, $ArC\underline{H}_2CH{=}C$), 4.40 (2H, s, $C{=}C(C)C\underline{H}_2OAc$), 5.52 (1H, dif. t, J=7.0 Hz, $CH_2C\underline{H}{=}C$)] in 19.3% yield. Hydrolysis of **8** afforded an alcohol (**10**) as colorless needles, $C_{15}H_{16}O_4$, mp 113—114°, [NMR ($CDCl_3$) δ: 3.58 (2H, d, J=7.0 Hz, $ArC\underline{H}_2CH{=}C$), 3.96 (2H, s, $C{=}C(C)C\underline{H}_2OH$), 5.47 (1H, dif. t, J=7.0 Hz, $CH_2C\underline{H}{=}C$)] in 82.5% yield. The presence of a primary alcoholic group in the structure of this product was confirmed by formation of an aldehyde (**11**) on oxidation with MnO_2 in $CHCl_3$ as colorless silky needles, $C_{15}H_{14}O_4$, mp 122—123°, [NMR ($CDCl_3$) δ: 9.31 (1H, s, $C\underline{H}O$)] in 78.6% yield. Although the geometrical configuration of **10** was expected to have an E-configuration from the reason described above, isomerization from this thermodynamically stable form to the unstable was accomplished by irradiation[6] of a solution of **10** in abs. benzene and gave **6** bearing a Z-configuration as colorless needles, $C_{15}H_{16}O_4$, mp 107—110° (lit.[2] mp 106—107°), [NMR ($CDCl_3$) δ: 3.59 (2H, d, J=8.0 Hz, $ArC\underline{H}_2CH{=}C$), 4.42 (2H, s, $C{=}C(C)$-$C\underline{H}_2OH$), 5.23 (1H, dif. t, J=8.0 Hz, $CH_2C\underline{H}{=}C$)] in 18% yield. This alcohol was identified with an authentic sample of the alcohol (**6**) prepared from **5** by hydrolysis by comparisons of infrared (IR), nuclear magnetic resonance (NMR) spectrum and thin-layer chromatography (TLC). This fact supported our assumption on the configurations of both synthetic specimens, because the Z-configuration of **6** derived from the natural coumarin was already well established due to an NOE experiment by Steck.[2] We, then, examined the transformation of osthenol (**2**) to arnottinin (**1**).

Treatment of osthenol acetate (**12**), $C_{16}H_{16}O_4$, mp 95—96°, with SeO_2 in Ac_2O gave a diacetate (**13**) as colorless prisms, $C_{18}H_{18}O_6$, mp 125—128°, [IR ν_{max}^{Nujol} cm^{-1}: no OH, 1758, 1727, 1719 sh (C=O); NMR ($CDCl_3$) δ: 2.04 and 2.34 (each 3H, s, $COCH_3$), 3.65 (2H, d, J=7.0 Hz,

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[5] Osthenol (**2**) and osthol (**7**) used in these experiments were prepared from commercial umbelliferone by the method developed by Taylor's and Murray's group, independently. [J. Hlubucek, E. Ritchie, and W.C. Taylor, *Tetrahedron Letters*, **1969**, 1369; *Chem. and Ind.*, **1969**, 1780; R.D.H. Murray, M.M. Ballantyne and K.P. Mathai, *Tetrahedron Letters*, **1970**, 243; *Tetrahedron*, **27**, 1247 (1971).

[6] The irradiation was performed with 120 W low pressure Hanovia mercurry lamp [external type, PIL-60 (Eicho Ltd., Osaka, Japan)].

ArC$\underline{H}_2$CH=C), 4.44 (2H, s, C=C(C)C$\underline{H}_2$OAc), 5.46 (1H, dif. t, $J=7.0$ Hz, CH$_2$C$\underline{H}$=C)] in 17.9% yield. It should be noted here that, in 1971, Bohlmann, *et al.*[7] accomplished the oxidation of osthenol (**2**) itself by the same procedure in the course of total synthesis of angenomalin (**14**), and obtained the diacetate having a different melting point (lit.[7] mp 105—106°). Therefore, we examined the oxidation of **2** with SeO$_2$, but obtained only **13** which was prepared from **12** in worse yield. Although Bohlmann did not mention about the configuration of their diacetate, an E-configuration of our diacetate (**13**) was exhibited by the following experiments. Hydrolysis of **13** gave **3** as colorless prisms, $C_{14}H_{14}O_4$, mp 157—159°, [NMR (CDCl$_3$) δ: 3.65 (2H, d, $J=7.0$ Hz, ArC$\underline{H}_2$CH=C), 3.91 (2H, s, C=C(C)C$\underline{H}_2$OH), 5.52 (1H, dif. t, $J=7.0$ Hz, CH$_2$C$\underline{H}$=C)] in 58% yield. Irradiation[6] of **3** in a mixed solvent (acetone/benzene=1/2) gave an isomerized alcohol, mp 193—196°, which was identified with arnottinin (**1**) by comparisons of IR, NMR, TLC and mixed mp. Furthermore, methylation of synthetic specimen **1** afforded a photoisomerized alcohol (**6**) prepared from osthol (**7**). These facts mentioned above established the structure of arnottinin as the structural formula **1**.

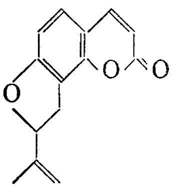

Chart 2

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[7] F. Bohlmann and H. Franke, *Chem. Ber.*, **104**, 3229 (1971).

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Chemische Untersuchungen der Inhaltsstoffe von *Pteris kiuschiuensis* Hieron.[1]

Im Zusammenhang mit der chemotaxonomischen Studien der Gattung *Pteris* und der verwandten Gattungen konnten aus *Pteris kiuschiuensis* Hieron. neben dem bereits bekannten Pterosin Q(I) drei neue Indan-1-on-Verbindungen, nähmlich Pterosin S(II), T(III) und U(IV) isoliert werden, deren Strukturen durch spektroskopische und CD-Daten aufgeklärt werden. In allen Fällen handelt es sich um Diastereoisomerengemische.

In Fortsetzung unserer chemischen und chemotaxonomischen Untersuchungen der Gattung *Pteris*, wurde unlängst *P. kiuschiuensis* Hieron. (jap. Name: Kohachijoshida) auf die Inhaltsstoffe untersucht. Die oberiridischen Teile dieser Pflanzen wurden mit Methanol extrahiert, der Extrakt in Wasser aufgenommen und nach einander mit Äther, Essigsäureäthylester und *n*-Buthanol ausgeschüttelt. Die jeden Phasen wurden dann durch Säulen- und anschliessende präparative Dünnschicht-Chromatographie an Kiesel-Gel gereinigt. Dabei aus der Essigsäureäthylester Phase wurden neben dem bereits von uns aus *P. oshimensis*