that the modified Polonovski reaction to afford **14** took place in the direction of carbon 3 while that to afford heteroyohimbine in the direction of carbon 21.

Hirsuteine (**3**) was oxidized with *m*-CPBA in a quantitative yield to the N-oxide (**6**) which was then submitted to modified Polonovski reaction followed by NaCNBH₃ reduction. The reaction products were separated to corynantheine (**15**, 51%) and a new base (**17a**, 22%; HClO₄ salt, mp 221–222°). The ultraviolet (UV) spectrum of **17a** was indolic and its mass spectrum exhibited M⁺ at *m/e* 368 indicating increase of 2 mass units from **3**. The presence of an ethyl group and C-3 βH in **17a** was revealed by the ¹HNMR spectrum [δ 0.89 (18 CH₃, t) and 4.10 (1H, broad s)]. From these spectral data, the structure of **17a** was estimated as 3-isocorynantheidine (**17a**). Subsequent epimerisation of C-3 H in hot acetic acid yielded corynantheidine (**17b**). Inversion of configuration at C-20 probably occurred in the protonation step to an enamine which was formed from **9b** by 1, 4 addition reduction with NaCNBH₃.

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Structural Establishment of Arnocoumarin and Arnottiacoumarin due to Chemical Modification of Marmesin and Rutaretin Methyl Ether¹⁾

New coumarins, arnocoumarin (**1**) and arnottiacoumarin (**2**), were isolated from *X. arnottianum* MAXIM. The structures of these coumarins were established by chemical transformation from marmesin (**7**) and rutaretin methyl ether (**10**) respectively.

Keywords—coumarin; *Xanthoxylum arnottianum*; Rutaceae; chemical transformation; pyrolysis; structural establishment

In the previous paper,²⁾ we reported isolation of two new coumarins (coumarin I, mp 180–183°, and coumarin II, mp 140–145°) together with thirteen other coumarins from *Xanthoxylum arnottianum* MAXIM. (Japanese name: Iwa-Zansho). In this communication, we wish to present the structural establishment of these two coumarins and formally designate them as arnocoumarin and arnottiacoumarin.

Arnocoumarin (coumarin I) (**1**) was obtained as colourless plates, mp 180–183°, C₁₄H₁₀O₃³⁾ [M⁺: *m/e* 266 (base peak)], IR $\nu_{\text{max}}^{\text{Nol}}$ cm⁻¹: 1730 (C=O), UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 273.5 (4.60), 296 (4.30) sh, 347 (4.03), in 0.00042% yield from the wood of *X. arnottianum*. The fact that two aromatic protons of **1** appear as two singlets in the NMR spectrum⁴⁾ indicates

- 1) This forms Part XXXVIII of "Studies on the Chemical Constituents of Rutaceous Plants" by H. Ishii, Part XXXVII; H. Ishii, E. Ueda, K. Nakajima, T. Ishida, T. Ishikawa, K.-I. Harada, I. Ninomiya, T. Naito, and T. Kiguchi, *Chem. Pharm. Bull.* (Tokyo), **26**, 864 (1978).
- 2) 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).
- 3) The compound gave satisfactory elemental analysis for the formula given.
- 4) NMR (CDCl₃) δ : 2.13 (3H, d, *J*=1.0 Hz, CH₃), 5.23 (1H, q, *J*=1.0 Hz, olefinic H), 5.82 (1H, s, olefinic H), 6.33 (1H, d, *J*=9.5 Hz, arom. H), 6.62, 7.37, and 7.55 (each 1H, s, arom. H), 7.74 (1H, d, *J*=9.5 Hz, arom. H).

that **1** should be a 6,7-disubstituted coumarin. It seems natural to suppose that **1** could be biogenetically derived *via* oxidative process from 7-demethylsuberosin (**3**), because **3** itself and many related coumarins [suberosin (**4**), peucedanol methyl ether (**5**), xanthyletin (**6**), marmesin (**7**), and xanthoarnol (**8**)], naturally occurred in the same plant.²⁾ This consideration and the inspection of the NMR spectrum⁴⁾ of **1** led us to propose a tentative structure (**1**) for arnocoumarin. Unfortunately, the amount of **1** was too minute to establish its structure by degradative procedure and, then, we tried to transform **7** to the compound having the formula (**1**).

Although all trials of dehydration by treatment of **7** with POCl₃ or by pyrolysis of several esters of **7**, *cis* elimination, resulted in giving a mixture of the *exo*- and *endo*-anhydromarmesin, refluxing of **7** in phenylisocyanate⁵⁾ gave *S-exo*-anhydromarmesin⁶⁾ (**9**), colourless plates, mp 119–121°, C₁₄H₁₂O₃³⁾ [NMR δ: 1.76 (3H, s, olefinic CH₃), 3.04 and 3.20 (each 1H, d.d.d, *J*=2.0, 8.0, and 16.0 Hz, ArCH₂CH), 4.95 and 5.08 (each 1H, d, *J*=2.0 Hz, olefinic H); [θ]₃₃₃ –3043 (MeOH)], as a sole product in 53.2% yield.

Chart 1

Chart 2

Oxidation of **9** with Hg(OAc)₂ gave the desired coumarin (**1**), colourless prisms, mp 179–183°, in 16.5% yield. This material was identical with a sample of the natural arnocoumarin.⁷⁾

On the other hand, arnottiacoumarin (coumarin II) (**2**) was isolated as slightly yellow needles, mp 140–145°, IR ν_{max}^{Nut} cm⁻¹: 1716 (C=O), in 0.00014% yield from the wood of the plant. The mass spectrum of **2** shows a base peak at *m/e* 256 corresponding to a parent ion of C₁₅H₁₂O₄, although the amount of **2** was too small to examine elemental analysis. Comparison of the NMR spectrum⁸⁾ of **2** with that⁴⁾ of **1** suggested that the former has a methoxy

- 5) W. Fenical and J.J. Sims, *Tetrahedron Lett.*, **1974**, 1137. The dehydration was performed without solvent. When used benzene as a solvent, the corresponding urethane was obtained in good yield.
- 6) T. Kikuchi, T. Yokoi, K. Umemoto, and T. Shingu, *Yakugaku Zasshi*, **94**, 1616 (1974). They reported isolation of a coumarin having the same plain structure from *Scaevola frutescens* (MILLER) KRAUSE (Goodeniaceae, Japanese name; Kusa-Tobera). However, the CD curve of their sample shows a positive Cotton effect in contrast to a negative one of our sample. This means that their coumarin should have an R-configuration because the chiral center of **7** has been established as S [I. Harada, Y. Hirose, and M. Nakazaki, *Tetrahedron Lett.*, **1968**, 5463; H. Ishii, F. Sekiguchi, and T. Ishikawa, *Tetrahedron*, in preparation.].
- 7) Kh. S. Mukhamedova, S.T. Akramov, and S. Yu. Yunusov, *Khim. Prir. Soedin*, **3**, 117 (1967) [*Chem. Abstr.*, **67**, 54284x (1967)]; Kh. S. Mukhamedova, *ibid.*, **1972**, 656 [*Chem. Abstr.*, **78**, 84595u (1973)]. They isolated a coumarin alkaloid designated as prangosine (**12**) from *Prangos pabularia*. **12** was converted to a derivative, hemiprangosine, which was depicted as the formula (**1**).
- 8) NMR (CDCl₃) δ: 2.13 (3H, d, *J*=1.0 Hz, CH₃), 4.31 (3H, s, OCH₃), 5.25 (1H, q, *J*=1.0 Hz, olefinic H), 5.83 (1H, s, olefinic H), 6.32 (1H, d, *J*=9.5 Hz, arom. H), 6.62 and 7.23 (each 1H, s, arom. H), 7.71 (1H, d, *J*=9.5 Hz, arom. H).

group instead of an aromatic proton of the latter. Taking the success of the structural establishment of **1** into consideration, the fact that rutaretin methyl ether (**10**) naturally occurred together with **7** in the same plant and has a methoxy group in its molecule instead of an aromatic proton of **7** stimulated us to synthesis of the compound having the structure (**2**) from **10** according to the procedure applied in the case of **7**. Treatment of **10** with phenylisocyanate gave the *exo*-anhydrorutaretin methyl ether (**11**), colourless prisms, mp 86–88°, $C_{15}H_{14}O_4$ ³⁾ [NMR δ : 1.77 (3H, s, olefinic CH_3), 3.06 and 3.23 (each 1H, d.d.d, $J=2.0, 8.0$, and 15.5 Hz, $ArCH_2CH$), 4.05 (3H, s, OCH_3), 4.95 and 5.10 (each 1H, d, $J=2.0$ Hz, olefinic H)], in 51.7% yield.

Oxidation of **11** with $Hg(OAc)_2$ gave colourless prisms, mp 139–143°, in 11.9% yield. This synthetic specimen was identical with a sample of arnottiacoumarin obtained from the natural source.

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Chemische Untersuchungen der Inhaltsstoffe von *Lindsaea ensifolia* Sw.¹⁾

Die oberirdischen Teilen von *Lindsaea ensifolia* Sw. enthalten neben einem bereits bekannten Flavon-C-Glykosid, Vitexin ein neuartiges Chromen-Derivat, Lindsaeasäure (I), deren Struktur durch spektroskopische Methoden aufgeklärt wird.

Keywords—*Lindsaea ensifolia*; Pteridaceae; vitexin; chromene; spectroscopic methods; structure; chemotaxonomy

In Fortsetzung unserer chemischen und chemotaxonomischen Untersuchungen der Gattung *Pteris* und der verwandten Gattungen wurde *Lindsaea ensifolia* Sw. (jap. Name: Inu-inomotoso, Fundort: Lien-hua-chi, Taiwan, China, Sammelzeit: Dezember, 1976) auf die Inhaltsstoffe untersucht. Die oberirdischen Teilen wurden mit Methanol extrahiert und der Extrakt säulenchromatographisch über Aktivkohle grob aufgetrennt (Elutionsmittel: MeOH, MeOH/ $CHCl_3$, 3:1, und $CHCl_3$). Die mit MeOH eluierte Fraktion wurde im Wasser suspendiert und nacheinander mit $CHCl_3$, Essigsäureäthylester und *n*-Butanol ausgeschüttelt. Der in Essigsäureäthylester übergegangene Teil wurde dann durch "Droplet Counter Current Chromatography" (DCCC, Lösungsmittelsystem: $CHCl_3/MeOH/H_2O$, 5:6:4) und anschließende Säulenchromatographie an Polyamid (Lösungsmittel: H_2O) gereinigt. Dabei wurde eine neue aromatische Säure (I) isoliert, für die wir den Namen Lindsaeasäure vorschlagen möchten und die vorliegende Arbeit beschäftigt sich mit ihrer Struktur-Aufklärung. Weiter wurde aus der bei der Aktivkohle-Chromatographie mit MeOH- $CHCl_3$ -Gemisch (3:1) eluierten

1) Chemische und chemotaxonomische Untersuchungen der Gattung *Pteris* und der verwandten Gattungen (Pteridaceae) XX. Mitteil., XIX. Mitteil.: T. Satake, T. Murakami, Y. Saiki, und C.-M. Chen, *Chem. Pharm. Bull.* (Tokyo), 26, 1619 (1978).