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 $NaCNBH_3$ reduction. The reaction products were separated to corynantheine (**15**, 51%) and a new base (**17a**, 22%; $HClO_4$ 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 ^{1}HNMR spectrum [δ 0.89 (18 $C\underline{H}_3$, 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 $NaCNBH_3$.

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Structural Establishment of Arnocoumarin and Arnottiacoumarin due to Chemical Modification of Marmesin and Rutaretin Methyl Ether[1]

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°, $C_{14}H_{10}O_3$[3] [M^+: *m/e* 266 (base peak)], IR ν_{max}^{Nujol} cm^{-1}: 1730 (C=O), UV λ_{max}^{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 spectrum[4] indicates

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[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).

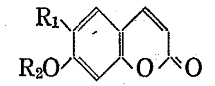
[2] H. Ishii, K. Hosoya, T. Ishikawa, and J. Haginiwa, *Yakugaku Zasshi*, **94**, 309 (1974); H. Ishii, K. Hosoya, T. Ishikawa, E. Ueda, and J. Haginiwa, *ibid.*, **94**, 322 (1974).

[3] The compound gave satisfactory elemental analysis for the formula given.

[4] NMR ($CDCl_3$) δ: 2.13 (3H, d, J=1.0 Hz, CH_3), 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).

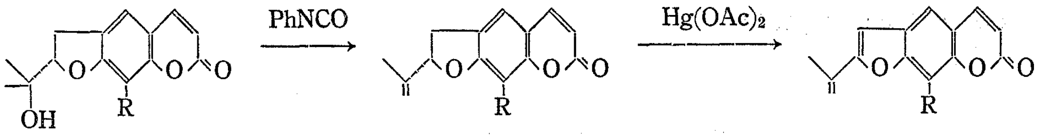
that **1** should be a 6,7-disubstituted coumarin. It seems natural to suppose that **1** could be biogenetically derived *via* oxidative process from 7-demethylsuberosin (**3**), because **3** itself and many related coumarins [suberosin (**4**), peucedanol methyl ether (**5**), xanthyletin (**6**), marmesin (**7**), and xanthoarnol (**8**)], naturally occurred in the same plant.[2] This consideration and the inspection of the NMR spectrum[4] 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 $POCl_3$ 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 phenylisocyanate[5] gave S-*exo*-anhydromarmesin[6] (**9**), colourless plates, mp 119—121°, $C_{14}H_{12}O_3$[3] [NMR δ: 1.76 (3H, s, olefinic CH_3), 3.04 and 3.20 (each 1H, d.d.d, $J=2.0$, 8.0, and 16.0 Hz, $ArC\underline{H}_2CH$), 4.95 and 5.08 (each 1H, d, $J=2.0$ Hz, olefinic H); $[\theta]_{333}$ −3043 (MeOH)], as a sole product in 53.2% yield.



3: $R_1=CH_2CH=C(CH_3)_2$; $R_2=H$
4: $R_1=CH_2CH=C(CH_3)_2$; $R_2=CH_3$
5: $R_1=CH_2\underset{OH}{C}H\text{-}\underset{OH}{C}(CH_3)_2$ $R_2=CH_3$
6: $R_1+R_2=(Ar)\text{-}CH=CH\text{-}C(CH_3)_2\text{-}(O)$
7: $R_1+R_2=(Ar)\text{-}CH_2\underset{C(OH)(CH_3)_2}{C}H\text{-}(O)$
8: $R_1+R_2=(Ar)\text{-}\underset{OH}{C}H\text{-}\underset{C(OH)(CH_3)_2}{C}H\text{-}(O)$

Chart 1



2: R=H
10: R=OCH_3

9: R=H
11: R=OCH_3

1: R=H
2: R=OCH_3

Ph=phenyl

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}^{Nujol} 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 $C_{15}H_{12}O_4$, although the amount of **2** was too small to examine elemental analysis. Comparison of the NMR spectrum[8] of **2** with that[4] of **1** suggested that the former has a methoxy

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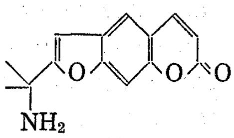
5) W. Fenical and J.J. Sims, *Tetrahedron Lett.*, **1974**, 1137. The dehydration was performed without solvent. When used benzene as a solvent, the corresponding urethane was obtained in good yield.

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, 54284*x* (1967)]; Kh. S. Mukhamedova, *ibid.*, **1972**, 656 [*Chem. Abstr.*, 78, 84595*u* (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**).



12

8) NMR ($CDCl_3$) δ: 2.13 (3H, d, $J=1.0$ Hz, CH_3), 4.31 (3H, s, OCH_3), 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, $ArC\underline{H}_2CH$), 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

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[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).