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Publisher: Taylor & Francis

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Agricultural and Biological Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tbbb19>

Lindenanolides in the Root of *Chloranthus japonicus* (Chloranthaceae)†

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Published online: 09 Sep 2014.

To cite this article: Satoshi Tahara, Yukiharu Fukushi, Jun Kawabata & Junya Mizutani (1981) Lindenanolides in the Root of *Chloranthus japonicus* (Chloranthaceae)†, *Agricultural and Biological Chemistry*, 45:6, 1511-1512

To link to this article: <http://dx.doi.org/10.1080/00021369.1981.10864738>

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Note

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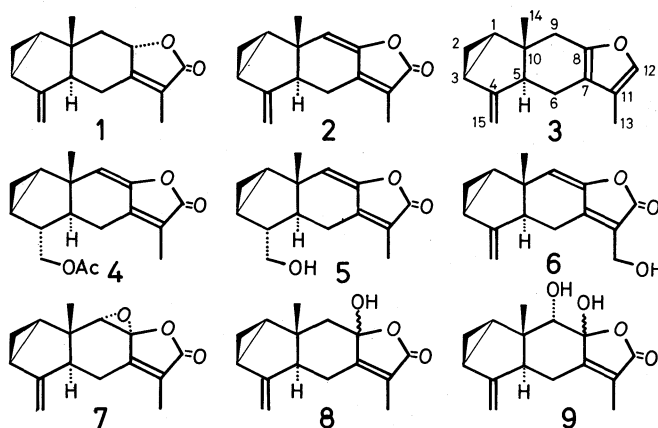
Received December 15, 1980

We have been investigating the constituents of *Chloranthus* plants, and hitherto isolated two sesquiterpene lactones, shizukanolide (**1**) and dehydro-shizukanolide²⁾ (**2**, identical to chloranthalactone A³⁾ in *Sarcandra glabra*), which are structurally related to lindenene (**3**) found in the root of *Lindera strychnifolia* by Takeda *et al.*⁴⁾ Compound **2** showed remarkable antifungal activity against *Mucor* and *Rhizopus* spp.¹⁾ Biogenetically interesting glechomanolid⁵⁾ and isofuranodiene^{6,7)} were also found in *C. japonicus*.¹⁾

Further survey resulted in the isolation of two other lindenanolides. Naturally occurring lindenanolides and lindenene (**3**) are depicted in Fig. 1. The fresh roots of *C. japonicus* (3.5 kg) were extracted with ether. The neutral constituents were chromatographed over Florisil (pretreated with 5% H₂O w/w). The ether/pentane (50~100%) fraction was subjected to rechromatography over Florisil (pretreated with 7% H₂O w/w). Elution with 50~60%

ether in pentane followed by concentration gave colorless prisms (**4**, 135 mg). Compound **4** was recrystallized from acetone: mp 157~158°C, $[\alpha]_D^{23} -144^\circ$ ($c=0.402$, CHCl₃). MS m/z (%): M⁺ 288 (4.5, C₁₇H₂₀O₄), 228 (25), 213 (100), 200 (13), 199 (11), 185 (26), 162 (12), 157 (14), 91 (28), 67 (11), 53 (11). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 282 (4.3). IR ν_{\max}^{KBr} cm⁻¹: 1770, 1730, 1640, 1235, 1225, 1020, 950, 820. NMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 0.90 (C₁₄-3H, s), 1.88 (C₁₃-3H, bs), 2.10 (CH₃CO-, s), 4.22 (C₁₅-2H, d, $J=6$ Hz), 6.22 (C₉-H, s). The NMR absorption pattern was considerably similar to that of chloranthalactone A except additional absorption of CH₃COOCH₂- and absence of the absorption band of the vinylidene group. The physicochemical properties of **4** were identical with those of chloranthalactone C which was recently isolated from *C. japonicus* and characterized by Uchida *et al.*³⁾

Successive elution with 60~70% ether in pentane and recrystallization from ether/pentane yielded another compound as needles (**5**, 103 mg). Compound **5**: mp 53.5~54.5°C, $[\alpha]_D^{23} -140^\circ$ ($c=0.408$, CHCl₃). High resolution MS: M⁺ m/z 246.1257 (C₁₅H₁₈O₃). MS m/z (%): 246 (29), 231 (47), 228 (M⁺-H₂O, 11), 215 (M⁺-CH₂OH, 24), 213 (100), 185 (39), 162 (39), 157 (36), 91 (78), 77 (36), 53 (40). IR ν_{\max}^{KBr} cm⁻¹: 3400 (broad, OH), 1770 (γ -lactone), 1635 (C=C), 1045, 1010 (C-O). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 282 (4.3). NMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 0.90 (C₁₄-3H, s), 0.6~1.0 (C₂-2H, m), 1.1~1.8 (C₁-H, C₃-H, C₄-H), 1.70 (C₁₅-OH, s, exchangeable with D₂O), 1.87 (C₁₃-3H, s), 2.1~2.6 (C₆-2H, m), 2.7 (C₅-H, m), 3.82 (C₁₅-2H, d, $J=6$ Hz), 6.22 (C₉-H, s). The UV spectra of **4** and **5** indicated that their chromophores were exactly identical. The molecular ion of **5** was smaller than that of **4** by 42 mass units (C₂H₂O). Moreover, IR and NMR spectra of **5** showed the presence of a hydroxymethyl group in place of an acetoxymethyl substituent found in **4**. Thus we estimated the structure of **5** to be a deacetyl derivative of **4**.

FIG. 1. Naturally Occurring Lindenanolides and Lindenene (**3**).

[†] Studies on the Chemical Constituents of Chloranthaceae Plants. Part II. For Part I, see ref. 1.

This estimation was further confirmed by the finding that acetylation of **5** gave **4** as described below. Acetylation of **5** was carried out in a mixture of acetic anhydride and pyridine, and yielded colorless prisms, mp 157~158°C. The IR spectrum of acetylated **5** coincided completely with that of **4**. MS m/z (%): 288 (M^+ , 4.6), 228 (26), 213 (100), 200 (12), 199 (11), 185 (26), 162 (13), 157 (13), 91 (26). The retention time on GLC (PEG-20M, 240°C, carrier gas N_2 22.5 ml/min) was 15.1 min, which agreed well with that of **4**. The specific optical rotation of acetylated **5**, $[\alpha]_D^{23} -112^\circ$ ($c=0.402$, $CHCl_3$), was quite similar to that of **4** (-114°). Thus the absolute configuration of **5** is concluded to be identical with that of **4**, as shown in Fig. 1.

Recently, Bohlmann *et al.*⁸⁾ reported the isolation and structure elucidation of another hydroxy-lindenanolide (onoseriolid, **6**). Chloranthalactones B (**7**), D (**8**) and E (**9**) were also found in *C. japonicus* by Uchida *et al.*³⁾

Antifungal activities of **4** and **5** against *Mucor griseocyanus* AHU 6044 were compared with that of chloranthalactone A (**2**), which is known to have high antifungal activity. In spite of the presence of an $\alpha\beta$, $\gamma\delta$ -unsaturated lactone moiety in the molecules of **4** and **5**, they were found to be substantially inactive.

Acknowledgments. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of

Education, Science and Culture (to S. T., No. 566057). The authors thank Dr. Takanori Kasai for help in measuring NMR, Miss Yuko Chiba for measuring MS, and Professor Shoichi Takao for providing the fungus.

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