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Lignans of *Trachelospermum liukiuense* and *T. foetidum*

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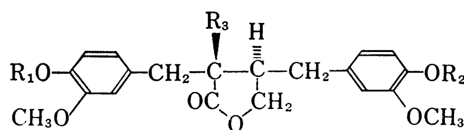
We have reported the isolations and structural elucidations of the five lignan glucosides, arctiin(I),[2)] matairesinoside(II),[2)] tracheloside(III),[2,3)] nortracheloside(IV)[3)] and arctigenin-4'-β-gentiobioside(V)[4)] as the main components of *Trachelospermum asiaticum* NAKAI var. *intermedium* NAKAI.



I : R_1=glucosyl, $R_2=CH_3$, R_3=H
II : R_1=glucosyl, R_2=H, R_3=H
III : R_1=glucosyl, $R_2=CH_3$, R_3=OH
IV : R_1=glucosyl, R_2=H, R_3=OH
V : R_1=gentiobiosyl, $R_2=CH_3$, R_3=H

Chart 1

The existence of the three *Trachelospermum* species besides *T. asiaticum* NAKAI var. *intermedium* NAKAI are known in Japan.[5)] Hereto there are a report on the morphological studies of *Trachelospermum* species by Hatsusima[5)] but no reports on the constituents of these species except our communication.[6)]

In this paper we should like to report the details of the isolations of the lignan glucosides from the stems of *T. liukiuense* HATUSIMA (Japanese name: Ryukyuteikakazura) collected in January 1970 at Yakushima and *T. foetidum* NAKAI (Japanese name: Muninteikakazura) collected in August 1969 at Ogasawara.

The extractions were carried out according to the procedure of *T. asiaticum* NAKAI var. *intermedium* NAKAI.

I, II, III and V from *T. liukiuense* HATUSIMA and I from *T. foetidum* NAKAI were isolated by column chromatographies of each of extracts with chloroform and ethyl acetate on silica gel as described in experimental section and identified with the authentic samples by infrared spectral (IR) comparisons and a mixed melting point, respectively. Also the presence of IV in *T. liukiuense* HATUSIMA and II, III, IV and V in *T. foetidum* NAKAI were detected by co-thin-layer chromatography (TLC) with the authentic samples.

The chemical differences from lignan glucosides of *T. asiaticum* NAKAI var. *intermedium* NAKAI were not found in the both of *T. liukiuense* HATUSIMA and *T. foetidum* NAKAI investigated.

Experimental

All melting points were not corrected. The following equipments were used: IR spectra, Infrared Spectrophotometer IRA-2 (Jasco); UV spectra, Hitachi Recording Spectrophotometer Model EPS-3T.

The TLC values were obtained with Kieselger G nach Stahl (Merck) as adsorbent; the spots were detected by spraying with 10% sulfuric acid and heating. For column chromatography silica gel (100 mesh, Mallinckrodt) was used.

Isolations of Lignan Glucosides from *T. liukiuense* HATUSIMA——The air-dried and cut stems (6 kg) were extracted four times with 20 liters each of hot MeOH. The MeOH solution was evaporated to small volume under reduced pressure, diluted with water and filtered. The filtrate was extracted successively with petr.

1) Location: *Tanabe-dori, Mizuho-ku, Nagoya, 467, Japan.*
2) I. Inagaki, S. Hisada, and S. Nishibe, *Chem. Pharm. Bull.* (Tokyo), **20**, 2710 (1972).
3) S. Nishibe, S. Hisada, and I. Inagaki, *Chem. Pharm. Bull.* (Tokyo), acceptd.
4) S. Nishibe, S. Hisada, and I. Inagaki, *Chem. Pharm. Bull.* (Tokyo), **21**, 639 (1973).
5) S. Hatsusima, *Shokubutsu Kenkyu Zasshi*, **16**, 20 (1940).
6) S. Nishibe, S. Hisada, and I. Inagaki, *Phytochemistry*, **10**, 3296 (1971).

ether, ether and $CHCl_3$ (5 times, 1 liter each). The $CHCl_3$ layer was evaporated to dryness. The aqueous layer was concentrated to syrup, which was extracted with hot AcOEt. The AcOEt layer was evaporated to dryness. The extracts with $CHCl_3$ (10.8 g) were subjected to a column chromatography, eluted by $CHCl_3$–EtOH (4: 1). The fractions (50 ml each) were monitored by co-TLC using $CHCl_3$–EtOH (4: 1) as developer and the corresponding one of five lignan glucosides as the reference sample. The fractions showing *Rf* value of arctiin were evaporated and the residue was recrystallized from AcOEt containing a small amount of water to give I (300 mg). The fractions showing *Rf* value of arctigenin-4′-β-gentiobioside were evaporated and the residue was recrystallized from MeOH to give V (39.3 mg). The other fractions did not give any crystalline material, though indicating the presence of II and III on TLC. Then the extracts with AcOEt (8.3 g) were subjected to a column chromatography, eluted by $CHCl_3$–EtOH (4: 1). The fractions (50 ml each) were monitored by co-TLC in a similar manner as the extracts with $CHCl_3$. I (105 mg) was obtained from the early fractions. The fractions showing *Rf* value of tracheloside were rechromatographed and the residue was recrystallized from EtOH to give III (190 mg). The fractions showing *Rf* value of matairesinoside were rechromatographed and the residue was recrystallized from AcOEt to give II (128 mg). The crystalline materials were not obtained from the fractions showing *Rf* value of nortracheloside, indicating the presence of a small amount of IV.

Arctiin (I)——Colorless crystalline powder, mp 109—112°. UV λ_{max}^{EtOH} nm(log ε): 230 (4.13), 280 (3.67). IR ν_{max}^{KBr} cm^{-1}: 3560—3240 (OH), 1765 (γ-lactone CO), 1605, 1590, 1510 (aromatic). *Anal.* Calcd. for $C_{27}H_{34}O_{11}\cdot 1.5H_2O$: C, 57.75; H, 6.60. Found: C, 57.54; H, 6.31.

I was identified with an authentic arctiin by IR and a mixed melting point.

Matairesinoside (II)——Colorless powder, mp 93—96°. UV λ_{max}^{EtOH} nm(log ε): 229 (4.21), 281 (3.81). IR ν_{max}^{KBr} cm^{-1}: 3600—3200 (OH), 1755 (γ-lactone CO), 1595, 1510 (aromatic). *Anal.* Calcd. for $C_{26}H_{32}O_{11}\cdot H_2O$: C, 57.98; H, 6.36. Found: C, 57.84; H, 6.62.

II was identified with an authentic matairesinoside by IR and a mixed melting point.

Tracheloside (III)——Colorless grains, mp 168—169°. UV λ_{max}^{EtOH} nm(log ε): 229.5 (4.26), 280 (3.84). IR ν_{max}^{KBr} cm^{-1}: 3560—3240 (OH), 1760 (γ-lactone CO), 1605, 1590, 1510 (aromatic). *Anal.* Calcd. for $C_{27}H_{34}O_{12}\cdot 1/2H_2O$: C, 57.95; H, 6.31. Found: C, 57.34; H, 6.31.

III was identified with an authentic tracheloside by IR and a mixed melting point.

Arctigenin-4′-β-gentiobioside (V)——Colorless crystalline powder, mp 174—176°. UV λ_{max}^{EtOH} nm (log ε): 230 (4.15), 280 (3.70). IR ν_{max}^{KBr} cm^{-1}: 3560—3200 (OH), 1770 (γ-lactone CO), 1605, 1590, 1510 (aromatic). *Anal.* Calcd. for $C_{33}H_{44}O_{16}\cdot 1/2H_2O$: C, 56.16; H, 6.28. Found: C, 56.21; H, 6.33.

V was identified with an authentic arctigenin-4′-β-gentiobioside by IR and a mixed melting point.

Isolation of Lignan Glucoside from *T. foetidum* NAKAI——The air-dried and cut stems (760 g) were extracted with hot MeOH. The MeOH solution was treated in a similar manner as that of *T. liukiuense*. The extracts with $CHCl_3$ (851 mg) were subjected to a column chromatography, eluted by $CHCl_3$–EtOH (4: 1) to isolate I. The extracts with AcOEt (236 mg) were subjected to a column chromatography, eluted by $CHCl_3$–EtOH (4: 1). The crystalline materials were not obtained from any fractions, though the presence of II, III, IV, and V was detected by co-TLC with the authentic samples.

Arctiin (I)——Colorless crystalline powder, mp 108—110°. UV λ_{max}^{EtOH} nm(log ε): 230 (4.18), 280 (3.70). IR ν_{max}^{KBr} cm^{-1}: 3560—3240 (OH), 1765 (γ-lactone CO), 1605, 1590, 1510 (aromatic). *Anal.* Calcd. for $C_{27}H_{34}O_{11}\cdot 1.5H_2O$: C, 57.75; H, 6.60. Found: C, 57.60; H, 6.56.

I was identified with an authentic arctiin by IR and a mixed melting point.

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