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Studies on the Chemical Constituents of *Acanthopanax chiisanensis* Nakai Roots

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Abstract□A lignan diglucoside, mp 240-242°, $C_{34}H_{46}O_{18}$, was isolated from the root cortex of *Acanthopanax chiisanensis* Nakai and it was identified as syringaresional diglucoside, Acanthoside D (Eleutheroside E).

Keywords□*Acanthopanax chiisanensis* (*Araliaceae*)-Indigenous plant-Folk medicine-syringaresinol diglucoside.

Acanthopanax chiisanensis Nakai is an indigenous plant of Korea, belonging to the Araliaceae family. Growing wild, its vertical distribution ranges from 200 to 1400m altitude, stretching from Mt. Chii across the entire Korean peninsula[1-2].

In the Asian region from ancient times, the root cortex or bark of *Acanthopanax* spp. has been known as *Acanthopanacis Cortex or Cortex Radicis*, and taken internally, is useful for evacuating pathologic abnormal factors within the body, for strengthening skeletal muscles and bones as a remedy for physical complaints through prolonged usage for the lightening and rejuvanation of the body. In Korea, it is still used for the cure of alleviation of rheumatism, palsy, hypertension, and diabetes[3~5].

Chemical studies on *Acanthopanax* spp. and *Eleutherococcus* spp. have been conducted [6~24]. From the root cortex of *Acanthospanax chiisanensis*, only polyacetylene series compounds and sesamin[25] have been identified, and from its leaves chiisanoside. Other medicinal properties on the sesamin and chiisanoside were not yet elucidated nn.

The componnd isolated in this experiment, was colorless, needle crystal which reacted positively to the Mäule and Anthron test.

On the basis of chemical and physicochemical evidence, it was identified as syringaresinol diglucoside, Acanthoside D (Eleutheroside E).

EXPERIMENTAL

Isolation of Syringaresinol diglucoside

Three kilograms of finely cut fresh root cortex of *Acanthopanax chiisanensis* Nakai was extracted three times with hot methanol. The extracts were collected and evaporated to dryness under reduced pressure.

Fatfree water fraction of MeOH extract was packed in Al_2O_3 column (Merck, Alumnium Oxide 90 active neutral column 3cm x 40cm) and elutriated with MeOH. The elutriate was collected and solvent was removed to obtain about 10g of the extract.This was dissolved in a miniumum volume of MeOH,

then 15g of silica gel was added to it and made a dough. The dough was then dried and packed in the upper part of silica gel column (Merck, Kiesel gel 60, column 2cm x 90cm) and elutriated with n-BuOH: EtOH: H_2O (5:2:3). When the fraction corresponding to R*f* 0.31 ($CHCl_3$: MeOH 4:1) was collected and concentrated, then allowed to stand to obtain the colorless crystal, mp. 240–242. This was positive to Mäule test.

Instruments and Analytical Conditions

Instruments used in this experinment and the physical conditions were as follows:

Melting point: PTC Melting Point Meter Model 304.5 was utilized and mp uncorrected.

Elemental Analysis: Perkin-Elmer 240 Elemental Analyzer.

Specific Rotatory: Rudolph Autopol TM–III Automatic Polarimeter was used and the material dissolved in pyridine at 20°C.

UV: Shimadzu Multi-purpose Recording Spectrophotomet PS 50L.

IR Analysis: Beckmann 18–A, Perkin Elmer 283.

PMR: Varian FT–80A NMR Spectrophotometer was used at 80MHz.

Mass analysis: JMS–D 300 JEOL MS Spectrophotometer. It operated at vacuum 10^{-6} torr, chamber V. 70ev., accal. v. 3kw, total emiss. 0.34 μA, chamber H. 180°, filament 4.6A.

Anal. calcd. for $C_{34}H_{46}O_{18}$: C, 54.9; H, 6.2, Found: 3, 54. 55; H, 0.06$[\alpha]_d^{20}$–33 (C= 2.0 pyridine).

UVλ_{max}^{EtOH} nm; 272, IRν_{max}^{KBr} cm^{-1}; 3,400 (OH), 2,930 (CH_2), 1,600. 1,530. 1,470. 790 (aromatic), 1,050 (C=0).

PMR: δ3.75 (12H, s, methoxhyl), δ6.8 (4H, s. aromatic).

Hydrolysis of Syringaresinol diglucoside

Fifteen milligrams of syringaresinol diglucoside was dissolved in 25 ml of mixed solution of 5% H_2SO_4 and MeOH (2:1), then hydrolyzed for 4 hours at 95°C. After the solvent was removed 15ml of distilled water was added. It was shaken out 3 times with small volume of $CHCl_3$, and the $CHCl_3$ soluble fraction was collected and washed with distilled water.

After the solvent was removed ethylacetate was added to solve it, It was allowod to stand for several days to form a crystal deposit with mp of 170–172 C. Anal. calcd. for C_{22} H_{26} O_8; C, 63.15; H 6.26, Found: C, 63.90; H, 6.51, MS (m/e) 154, 155, 161, 167 , 181, 182, 193, 209, 210, 235, 236, 418.

This compound shows the R*f* value 0.9 by TLC. This corresponds to the R*f* value of the authentic syringaresinol and no depression was noticed in the mixed melting point with authentic syringaresinol.

Glucose Analysis in the Hydrolysate of Syringaresinol diglucoside

The hydrolysate of syringaresinol diglucoside, from which the syringaresinol has been separated, was neutrized by $Ba(OH)_2$ and analyzed chromatographically on paper in the system of n–butanol-acetic acid- water (4:1:5). Only glucose (R*f* 0.18) was identified in this case.

To determine the glucose content of syringaresinol diglucoside, accurately weighed sample (15mg) of syringaresinol diglucoside was dissolved in 6ml of mixture of 5% acid

and methanol (2:1) and hydrolyzed for 5 hours at 100°C. The hydrolysate was neutralized. The volume of the solution obtained was made up to 24 ml with distilled water and titrated as described by Somogyi.[29~30]. The content of glucose in the glycoside is 43.67%.

RESULTS

A colorless, needle crystal, C_{34} H_{46} O_{18} mp; 240–242°, $[\alpha]_D^{20}$; -33 (C=2.0 pyridine) was isolated from the methanolic extract of root cortex of *Acanthopanax chiisanensis* Nakai. The colorless, needle crystal was positive to Mäule and anthron test, thus revealing one of lignan glycosides. This glycoside was identified as syringaresinol diglucoside (Acanthoside D) by IR, NMR, MS spectrometry, and surgar analysis. The spectra were identical with authentic specimen, which was isolated from the root cortex of *Eleutherococus senticosus*.[28]

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