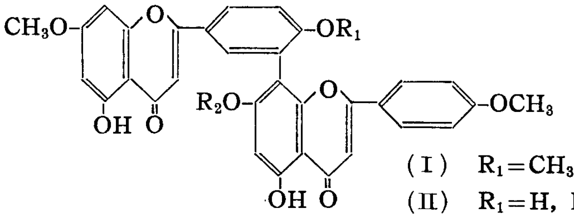
UDC 547.972.2/.3:582.475

149. **Nobusuke Kawano** : Studies on the Structure of Sciadopitysin, a Flavonoid from the Leaves of *Sciadopitys verticillata* Sieb. et Zucc. (8)*1

(*Pharmaceutical Faculty, University of Nagasaki**2)

In the preceding paper[1] it was reported that sciadopitysin should be represented by formula (I) or (II) and that in order to elucidate this alternative, degradation of sciadopitysin triethyl ether was carried out.



(I) $R_1=CH_3$, $R_2=H$
(II) $R_1=H$, $R_2=CH_3$

Sciadopitysin triethyl ether was decomposed in a boiling methanolic barium hydroxide solution by the same procedure as for sciadopitysin trimethyl ether[2] to give anisic acid, 2-hydroxy-4-methoxy-6-ethoxyacetophenone, and a phenolic acid, $C_{20}H_{20}O_7$, m.p. 258~259°(decomp.), which was considered to correspond to substance B,[1,2] and oxidized with a potassium permanganate solution into 4-methoxyisophthalic acid. From this result the structure of sciadopitysin can definitely be represented by formula (I). Therefore, the degradation of sciadopitysin triethyl ether (III) is represented as in Chart 1. This evidence is also compatible with a 3′—6″ bisflavonoid structure, but the 3′—8″ structure (III) is preferred as mentioned in the preceding paper.

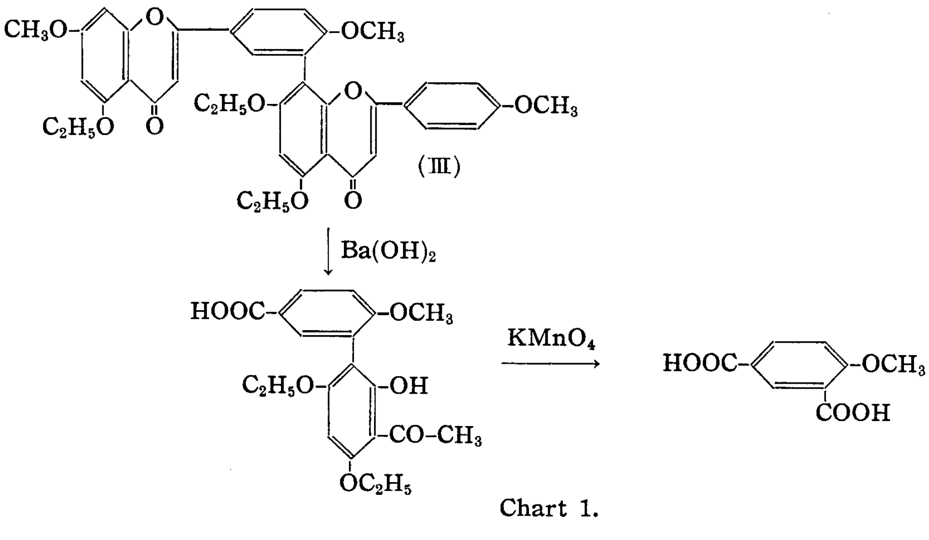


Chart 1.

Grateful acknowledgement is offered to Dr. T. Kariyone for his interest and encouragement throughout this work. Thanks are also due to Mr. H. Miura for his technical assistance and to Miss H. Ohta for elemental analytical data. The author also acknowledges a Grant-in-Aid for Scientific Research from the Ministry of Education.

---

*1 This paper constitutes Part XXXVII of "Chemical Constituents of the Plants of Coniferae and Allied Oders" by T. Kariyone (Part XXXVI : Footnote 1).

*2 Showa-machi, Nagasaki (河野信助).

1) Part (7) : This Bulletin, **7**,698(1959).

2) Part (6) : Yakugaku Zasshi, **79**, 1182(1959).

Experimental*[3]

Sciadopitysin Triethyl Ether (III)—To a mixture of finely powdered sciadopitysin (1 g.) and Et_2SO_4 (6 cc.) 30% KOH solution (12 cc.) was added dropwise by the same procedure as for methylation,[3] warming the mixture sometimes because of less reactivity of Et_2SO_4 than Me_2SO_4. The reaction mixture was washed repeatedly with water, dissolved in warm EtOH (5 cc.), and cooled to give crystals. Filtered and washed crystals were recrystallized from a large amount of EtOH because of its slight solubility, giving pale yellow prisms (0.6 g.), m.p. 209~210°. When heated very slowly it melted at 253~254° (reported[4] m.p. 244~245°). *Anal.* Calcd. for $C_{39}H_{36}O_{10}\cdot H_2O$: C, 68.61; H, 5.61. Found : C, 68.38; H, 5.43.

Degradation of Sciadopitysin Triethyl Ether in Methanolic $Ba(OH)_2$ Solution—A mixture of sciadopitysin triethyl ether (0.68 g. = 1 millimole) and *N* methanolic $Ba(OH)_2$ solution (450 cc.) containing 71 g. of $Ba(OH)_2\cdot 8H_2O$ was refluxed on a steam bath during 20 hr., by which the substance dissolved gradually to give an orange yellow solution. One-half volume of MeOH was distilled off and water (300 cc.) was added. The rest of MeOH was evaporated *in vacuo*, HCl (15 cc.) was added, and $BaCO_3$ was filtered off. The yellow filtrate was acidified with 20% HCl, allowed to stand overnight, and filtered (Filtrate 1). White deposit was warmed with 10% $NaHCO_3$ solution (30 cc.), cooled, and filtered (Filtrate 2). Yellow crystals obtained were recrystallized from EtOH, giving faint cream needles, m.p. 132~133° (reported,[5] m.p. 133~134°). Yield, 170 mg. (0.81 millimole). *Anal.* Calcd. for $C_{11}H_{14}O_4$ (2-Hydroxy-4-methoxy-6-ethoxyacetophenone) : C, 62.84; H, 6.71. Found : C, 62.61; H, 6.77.

Filtrate (2) was acidified and filtered (Filtrate 3). The precipitate obtained was warmed with EtOH (10 cc.), cooled, and filtered (Filtrate 4), leaving colorless minute crystals, which were recrystallized from acetone to colorless needles, m.p. 258~259°. Yield, 260 mg. (0.70 millimole). *Anal.* Calcd. for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found : C, 64.29; H, 6.09.

Filtrate (1) and (3) were combined and extracted three times with ether. The combined ether layer was dried and evaporated, leaving a crystalline residue. Filtrate (4) was evaporated to dryness, combined with this residue and recrystallized from water to colorless needles, m.p. and mixed m.p. 180~182°. Yield, 120 mg. (0.79 millimole) of anisic acid.

Oxidation of the Phenolic Acid, $C_{20}H_{22}O_7$—The foregoing phenolic acid (190 mg.) was dissolved in 1% NaOH solution (20 cc.) and $KMnO_4$ (0.8 g.) was added under stirring at 70~80° during 1 hr. After further 2 hr.'s stirring at this temperature, the reaction mixture was treated in the same way as described before[1] on the oxidation of substance B and gave an acid (20 mg.) as colorless prisms (from AcOEt), m.p. 263~264°. It was identified with 4-methoxyisophthalic acid by admixture.

Summary

The structure of sciadopitysin, $C_{33}H_{24}O_{10}$, was deduced to be a new-type bisflavonoid of formula (I) on the basis of the degradation product of its triethyl ether (III).

(Received April 20, 1959)

---

*[3] All m.p.s are uncorrected.

[3] T. Kariyone, N. Kawano : Yakugaku Zasshi, **76**, 450(1956).

[4] T. Kariyone, T. Sawada : *Ibid.*, **78**, 1018(1958).

[5] A. Sonn : Ber., **61**, 2302(1928).