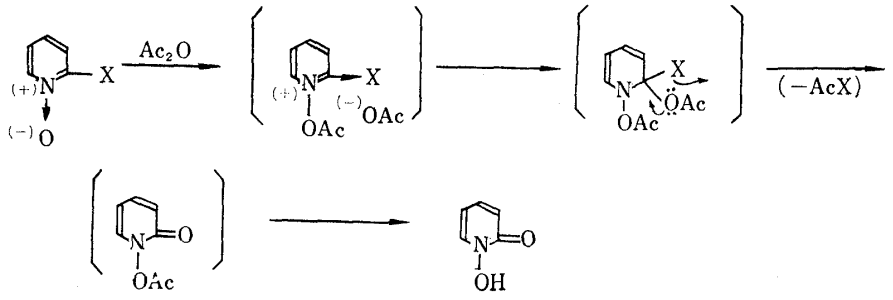

Schema 3.

Die von uns ausgeführten Versuche zeigen, dass diese Reaktion auf Pyridazinderivaten anwendbar und überdies ein von Hamana[3] befürworteter Mechanismus richtig ist.

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Isolation and Structure of New Diterpenes, Dimethylsciadinonate and Sciadinone, from *Sciadopitys verticillata*[1]

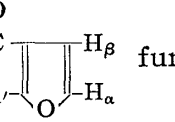
Recently, M. Sumimoto *et al.*[2] have proposed the structure I for furanoid diterpene, sciadin, $C_{20}H_{24}O_4$, m.p. 160°, $[\alpha]_D$ +10.3°, which had been isolated from the heartwood of *Sciadopitys verticillata* ZIEB. et ZUCC.

The authors now wish to report the isolation from the leaves of the same plant two other new furanoid diterpenes for which the names, dimethylsciadinonate and sciadinone are proposed, their structural determination, and correlation of these compounds with sciadin.

From the fraction of the methanol extract indistillable with steam,[1] the following three crystalline compounds were isolated through chromatography on silica gel, dimethylsciadinonate (II), m.p. 122°, $[\alpha]_D$ −45.0 (in $CHCl_3$), UV λ_{max}^{EtOH} mμ (log ε) : 203 (4.318), 255 (3.600); IR ν_{max}^{KBr} cm^{-1} : 1730 (ester), 1689 (conjugated carbonyl), 1647 (C=C), 1592, 1568, 1508 (furan), 879 (exocyclic methylene), 873 (furan), 822, 766 (*Anal.* Calcd. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27; O, 24.71; mol. wt., 388.4. Found : C, 68.03; H, 7.26; O, 24.80; mol. wt., 361); sciadinone (III), m.p. 207°, $[\alpha]_D$ −59.9° (in $CHCl_3$); UV λ_{max}^{EtOH} mμ (log ε) : 201 (4.277), 254 (3.623); IR ν_{max}^{KBr} cm^{-1} : 1730 (lactone), 1674 (conjugated carbonyl), 1642 (C=C), 1606, 1563, 1517 (furan), 893 (exocyclic methylene), 872 (furan), 841, 749 (*Anal.* Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37; O, 19.49. Found : C, 73.00; H, 7.32; O, 19.75); sciadin,

1) M. Ishikawa, T. Tsuchiya : Gas chromatographic analysis of the steam distillable parts of this fraction was reported in the Repts Res. Inst. Dental Materials, Tokyo Medico-Dental University, **2**, 401 (1962).
2) M. Sumimoto, Y. Ito, H. Yokoi : Abstract of Papers, Symposium on the Organic Chemistry of Natural Products, Sapporo, Japan (1962).

m.p. 158~159°, $[\alpha]_D$ +13.77° (in $CHCl_3$) : UV λ_{max}^{EtOH} mμ (log ε) : 205 (4.022); IR ν_{max}^{KBr} cm^{-1}: 1742, 1636, 1607, 1507, 895, 875 (*Anal.* Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37; O, 19.49. Found : C, 73.31; H, 7.36; O, 19.45). The latter sciadin showed no depression of m.p. on admixture with the one obtained from the heartwood of the same plant and their IR spectra were superimposable.[3] Unlike sciadin, which has a non-conjugated furan ring, ultraviolet and infrared spectra of II and III strongly suggest the existence of furan ring conjugated with carbonyl group in these two compounds. The presence of a ketone group in II was confirmed through the formation of its 2,4-dinitrophenylhydrazone, m.p. 152~154°, UV : λ_{max}^{EtOH} 367 mμ (log ε, 4.258); IR ν_{max}^{KBr} cm^{-1} : 1723, 890 (*Anal.* Calcd. for $C_{28}H_{32}O_9N_4$: C, 59.14; H, 5.67; N, 9.85. Found : C, 59.19; H, 5.48; N, 10.01). Although the preparation of 2,4-dinitrophenylhydrazone was only successful with II, nuclear magnetic resonance spectra of both compounds clearly show the presence of



function[4] (for dimethylsciadinonate (II), $H_{\alpha'}$, 1.93; H_α, 2.56; H_β, 3.22; for sciadinone (III), $H_{\alpha'}$, 1.86; H_α, 2.58; H_β, 3.29).[5]

Occurrence of II, III, and sciadin in the same plant, and the presence of a furan-ring and an exocyclic methylene in common, indicate a close relationship to exist among them. Structural correlation among these three compounds was established in the following manner. Reduction of II with $LiAlH_4$ gave an amorphous product,*1 which on oxidation with pyridine-chromium trioxide gave rise to two isomeric ketolactones, IV, m.p. 154~155°, $[\alpha]_D$ −61.67° (in $CHCl_3$), IR ν_{max}^{KBr} cm^{-1} : 1738, 1670, 1649, 1518, 884, 870. (*Anal.* Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37; Found : C, 73.54; H, 7.35), and the other ketolactone, m.p. 207° (*Anal.* Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found : C, 73.03; H, 7.64), in the yield of 46.9% and 6.5%, respectively, with a trace of sciadin.*2 The latter compound melting at 207° was proved to be completely identical with sciadinone (III) through mixed melting point and comparison of their infrared spectra. Through the same reaction sequence *via* triol, m.p. 129~131°, IR ν_{max}^{KBr} cm^{-1} : 3600~3200, 1637, 1595, 1503, 892, 885, 873 (*Anal.* Calcd. for $C_{20}H_{30}O_4 \cdot \frac{1}{2}H_2O$: C, 69.94; H, 9.10. Found : C, 70.48; H, 9.31), sciadin afforded IV and III, with the starting compound,*2 approximately in the same ratio, as was the case in II. Since the structure I has been proposed for sciadin, ketolactone IV and sciadinone should be assigned structures IV and III, respectively, or visa versa. Unambiguous choice of structure III for sciadinone was established through the following experiments. Sciadin was heated with excess of KOH-methanol solution and evaporation of the solvent *in vaccum* gave powderly potassium sciadinate (V), which was reduced with $NaBH_4$ in aqueous methanol at room temperature. Acid treatment, followed by chromatography over silica gel afforded the recovered sciadin (I) in 51% yield and glassy hydroxylactone (VI), IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3600, 1722, 1648, 1596, 903, 876, in 40% yield. Without further purification, hydroxylactone (VI) was subjected to oxidation with chromium trioxide in pyridine to give a crystalline compound melting at 207°. The

*1 The amorphous product is possibly a mixture of epimers of hydroxyl group at C-12. Its acetate showed two peaks (R.R.T. 0.57 and 0.89) in the gas chromatogram. The latter R.R.T. was coincident with that of the triol acetate obtained from sciadin. cf. foot note 6).

*2 In both cases of the chromatographic separation over alumina of the oxidation products via triols, the final eluates indicated the presence of trace of sciadin, through analyses by thin layer chromatography on Silica gel G "Merck" (Rf-value 0.59, hexane-ether : 1:1) and gas chromatography (R.R.T. 0.77). cf. foot note 6).

3) The authors are grateful to Dr. M. Sumimoto, Dept. of Agriculture, Kyushu University, for the gift of the authentic sample of sciadin.

4) For the numberring system, cf. J. Cocker, T. Halsall : J. Chem. Soc., **1956**, 4262.

5) Nuclear magnetic resonance spectra were obtained in chloroform solution by Varian DP 60 Spectrometer operated at 60 Mc. The chemical shifts are given in τ-unit.

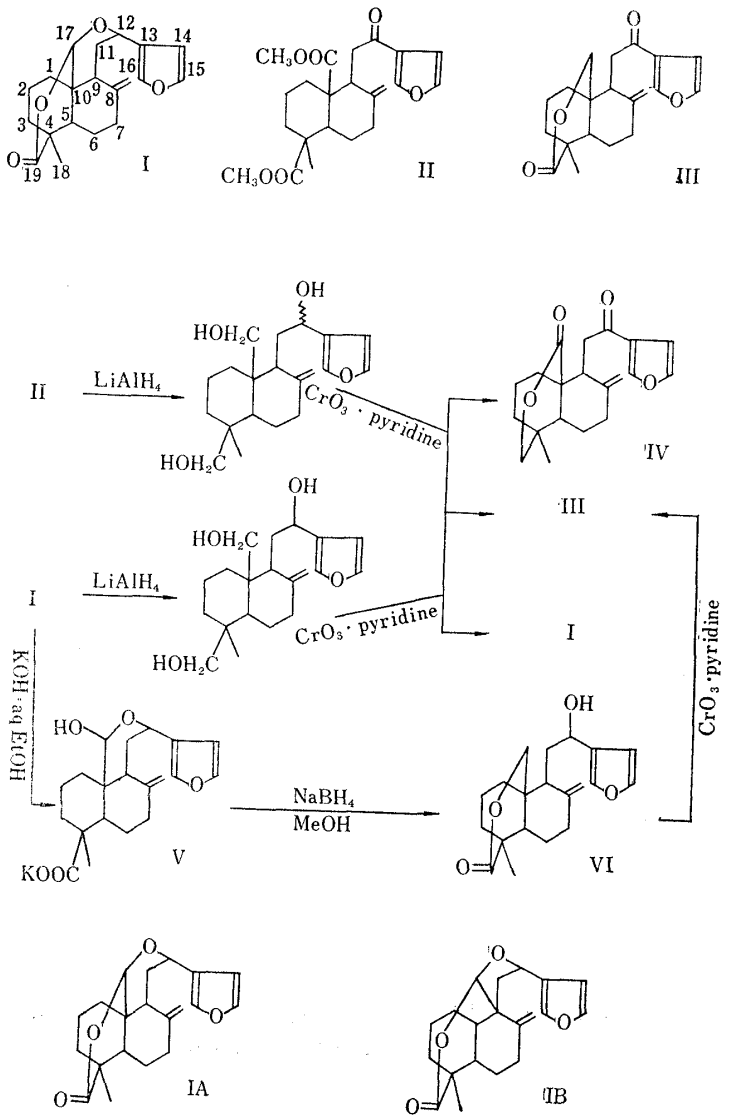


Chart 1.

identity of this compound with sciadinone (III) was established through mixed melting point and their superposable infrared spectra.

The absence of IV in the oxidation product was confirmed through thin layer chromatography on silica gel and by gas chromatography.[6] Thus, the structure of sciadinone was firmly established as III, and the structure for ketolactone melting at 155°, therefore, was proved to be IV. Since the above reaction sequences have revealed that dimethylsciadinonate (II) possesses the same carbon skeleton as sciadinone (III) and sciadin (I), the structural formula II has been assigned to dimethylsciadinonate from the consideration of its nuclear magnetic resonance spectrum, on which a singlet at 6.38 of six protons area intensity shows definitely the presence of two methoxycarbonyl groups. Thus, sciadin, dimethylsciadinonate, and sciadinone were correlated, but the structure of sciadin itself deserves a brief comment. Whereas Sumimoto's experiments and the

6) Gas chromatography was conducted on the following conditions: Apparatus, Schimadzu GC-1B, HFD-1; column, 6 mm × 150 mm; 1% SE-30 on chromosorb w; column temp., 230°; flash heater temp., 280°; N_2 pressure, 2 Kg., 30 ml./min.; H_2 pressure, 0.8 Kg., 35 ml./min. The relative retention times were calculated based on that of progesterone as a reference, I, 0.77; II, 0.62; III, 0.91; IV, 0.68.

authors' were consistent with the proposed structure IA, information available was insufficient for the structure to be considered fully established, because an alternative structure IB could not be excluded. The alternate structure IB was abondoned for the following reasons. In nuclear magnetic resonance spectrum, ketolactone IV shows octet peaks in the region of 5.92~6.87 analysed as AB parts of ABX system (τ_A; 6.14, τ_B; 6.66, J_{AB}; 17.4 c.p.s., J_{AX}; 8.7 c.p.s., J_{BX}; 4.0 c.p.s.). Nuclear magnetic resonance spectra of IV, as well as those of its related compounds (I, II, and III), indicate that these octet peaks mentioned above originated from the two methylene protons on C-11 adjacent to the carbonyl carbon C-12, and furthermore, this methylene group is neighboured by methine function (C-9-H). Since the structure IB has been eliminated spectroscopically as shown above, sciadin, dimethylsciadinonate and sciadinone have been proved to have the structure IA, II, and III, respectively.

The authors express their gratitude to Mr. Y. Kawazoe and Mr. H. Hotta, Facnety of Pharmaceutical Sciences, Tokyo University, for the interpretation of NMR spectra. They also express their deep thanks to Tokyo University Forests for the gift of the materials.

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The Mechanism of the New Color Reaction of Anthrone with Furfural and Pentose

The studies on the color reaction of anthrone with carbohydrate introduced by Dreywood[1] have been reported by many investigators. Sattler and Zerban,[2] Shriver, Webb, and Swanson,[3] and Yemm and Willis[4] assumed from the results of spectrophotometrical studies that the color was due to furfural compound derived from carbohydrate by strong acid. On the other hand, Momose, *et al.*[5] isolated one of the main dyes as trianthronylidenepentane from the reaction mixture of anthrone with pentose or hexose, and discussed a new reaction mechanism without the formation of furfural compound.

Recently the authours have reported in the preceding paper[6] that furfural gave a specific blue color with anthrone when the reaction mixture was cooled enough to keep away from the evolution of heat. When pentose was previously heated in concentrated acid in the absence of anthrone, it also gave the same blue color with anthrone, thongh pentose itself gave no color without heating. As this specfic color was very unstable by heat, the reaction mixture should be kept in cold. The intensity of the blue color

1) R. Dreywood : Ind. Eng. Chem., Anal. Ed., **18**, 499 (1946).
2) L. Sattler, F. W. Zerban : Science, **108**, 207 (1948).
3) E. H. Shriver, M. B. Webb, J. W. Swanson : TAPPI., **33**, 578 (1950).
4) E. W. Yemm, A. J. Willis : Biochem. J., **57**, 508 (1954).
5) T. Momose, Y. Ueda, K. Sawada, A. Sugi : This Bulletin, **5**, 31 (1957).
6) R. Sawamura, T. Koyama : Yakugaku Zasshi, **81**, 1689 (1961).