Phenolic Compounds in Living Tissues of Woods VIII.* Olivil from the sapwood of yachidamo

Fraxinus mandshurica RUPR. var. *japonica* MAXIM.**

By

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樹木の生活組織のフェノール成分 VIII*

ヤチダモ辺材からのオリビール**

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Abstract

The compound SE-1, which had been isolated from the sapwood of yachidamo (*Fraxinus mandshurica* RUPR. var. *japonica* MAXIM.) together with (±) -syringaresinol (I) and fraxinol (II), was identified to be olivil (III) by ^{1}H-NMR and MS spectroscopies.

The specific rotation of the compound SE-1 was $[\alpha]_D$ −56.0° and that of an authentic olivil given by Dr. Ayres was $[\alpha]_D$ −38.0°. They were not exactly same even though measured in the same condition. However, the values were similar each other.

Since SE-1 (olivil) was not detected in the heartwood, it might convert into other compounds such as cycloolivil (VIII) during the heartwood formation.

Key words: Olivil, sapwood, heartwood formation, glycosides, *Fraxinus*.

Contents

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1. Introduction

In the previous work[1], three phenolic compounds SE-1, SE-2 and SE-3 were isolated from the sapwood extractives of yachidamo (*Fraxinus mandshurica* RUPR. var. *japonica* MAXIM.) and the latter two compounds were identified to be (±) − syringaresinol (I) and fraxinol (II), respectively. One of them SE-1 has not been ascertained to date although it was characterized as a lignan.

This paper deals with the structural elucidation of the compound SE-1 by ^{1}H-NMR and MS spectroscopies.

2. Results

2.1 Structure of the compound SE-1 (olivil)

The molecular ion peak of SE-1 in the high mass spectrum appears at m/z 376.2534 and it attributes the formula $C_{20}H_{24}O_7$ (Teble 1). However, the calculated elementary composition was rather different from that of the found (See **5. 2. 1**). The cause of the difference was clarified by its ^{1}H-NMR spectrum. The ^{1}H-NMR spectrum of SE-1 (in d_6-DMSO) showed two signals (at δ 1.05 and 3.60) originated from a mole of ethanol. The ethanol was contained as solvent of crystallization in the compound SE-1. Considering the above result, the elementary compositions of the calculated and of the found ones well coincided with each other.

Methylation of SE-1 with diazomethane (CH_2N_2) gave a dimethyl ether (V) and methylation with dimethyl sulfate gave a tetramethyl ether (VI). This indicates that SE-1 has four hydroxyl groups and two of them are phenolic or enolic hydroxyl groups and the other two are alcoholic hydroxyl groups.

Acetylation of SE-1 with pyridine and acetic anhydride at 55 ± 2°C for 8 hr yielded a tetraacetate (IV). Fig. 1 shows the ^{1}H-NMR spectrum of SE-1 tetraacetate (IV). It shows the existence of methyl protons of the tertiary alcohlic acetoxyl group at δ 1.80 in addition

Table 1. High mass spectral data of olivil (SE-1, III)

OBSD.	CALCD.	ERROR	FORMULA	INT.
m/z 376.1534	.1522	+1.2	$C_{20}H_{24}O_7$	40% M^+
303.0546	.0504	+4.1	$C_{15}H_{11}O_7$	22
239.0934	.0919	+1.4	$C_{12}H_{15}O_5$	34
238.0868	.0841	+2.6	$C_{12}H_{14}O_5$	35
221.0829	.0813	+1.5	$C_{12}H_{13}O_4$	34
209.0825	.0813	+1.1	$C_{11}H_{13}O_4$	32
208.0729	.0735	−0.5	$C_{11}H_{12}O_4$	26
207.0685	.0657	+2.8	$C_{11}H_{11}O_4$	26
181.0857	.0864	−0.6	$C_{10}H_{13}O_3$	27
180.0778	.0786	−0.8	$C_{10}H_{12}O_3$	38
165.0725	.0759	−3.3	$C_{10}H_{11}O_2$	42
153.0517	.0551	−3.4	$C_8H_9O_3$	54
151.0380	.0395	−1.4	$C_8H_7O_3$	50
139.0723	.0759	−3.5	$C_8H_{11}O_2$	47
138.0663	.0680	−1.7	$C_8H_{10}O_2$	63
137.0594	.0602	−0.8	$C_8H_9O_2$	58

to those of the primary alcoholic acetoxyl group at δ 2.05. The signal at δ 2.29 are those of two phenolic acetoxyl groups. These data support the assumption on the hydroxyl groups obtained in methylation of SE-1 as described above.

Two singlets at δ 3.79 and 3.82 indicate that SE-1 has two aromatic methoxyl groups. The singlet at δ 2.29 derives from six protons of two phenolic acetoxyl groups. The multiplet in the region δ 7.15-6.58 corresponds to six protons of the two aromatic nuclei. The fragment ion of SE-1 at m/z 137 in its mass spectrum is originating from the hydroxymethoxybenzyl group (Table 1). Oxidation of the SE-1 dimethyl ether (V) with permanganate yielded veratric acid (VII). These data of spectroscopies and degradation indicated that SE-1 has two guaiacyl nuclei.

The subtraction of two guaiacyl groups $C_{14}H_{14}O_4$ from the molecular formula $C_{20}H_{24}O_7$ of SE-1 gives the $C_6H_{10}O_3$ moiety. It is evident from the NMR spectrum (Fig. 1) that two of the three oxygen atoms in the partial structure $C_6H_{10}O_3$ are of those of the primary and the tertiary alcoholic hydroxyl groups. The residual one oxygen is considered to be alloted for one ether linkage since the IR spectrum of SE-1 showed no

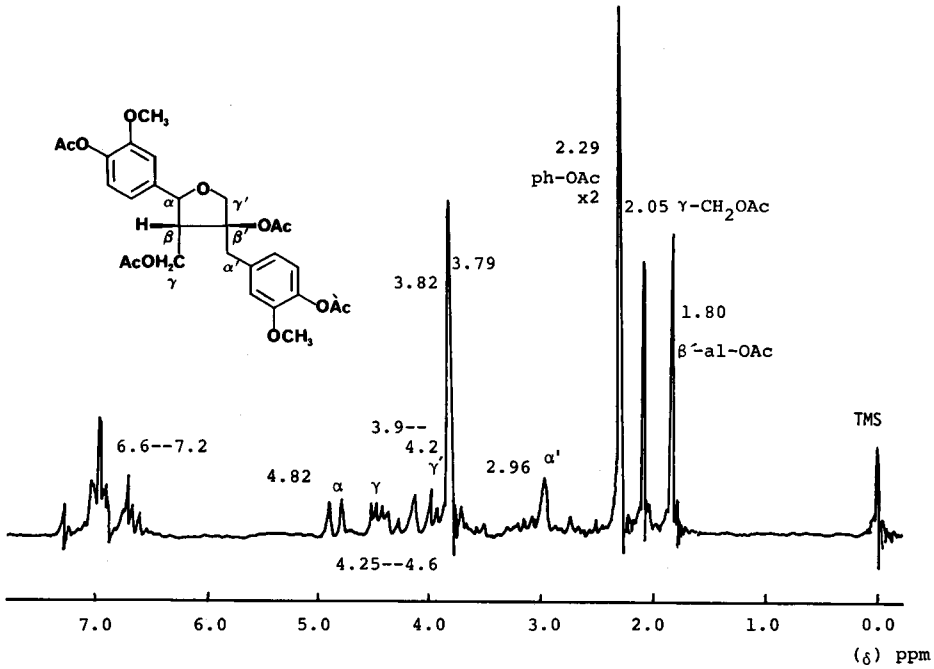

Fig. 1. ^{1}H-NMR spectrum of SE-1 (olivil) tetraacetate (IV) in $CDCl_3$.

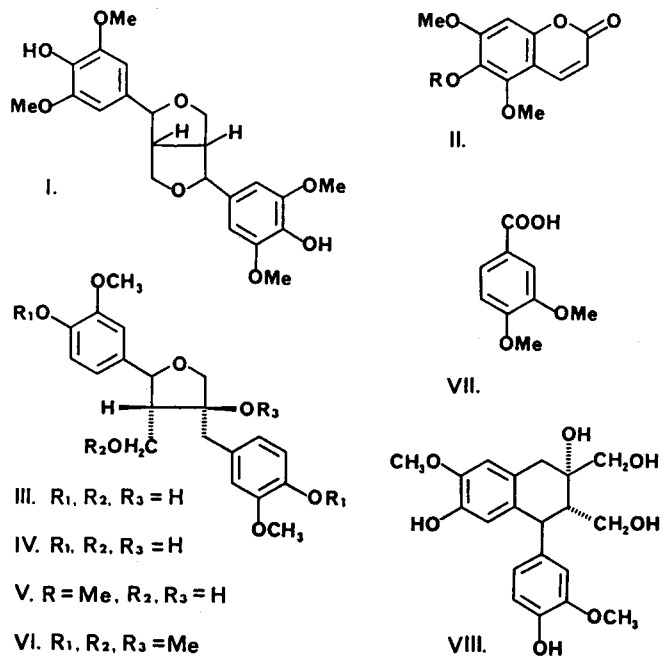

Chart A

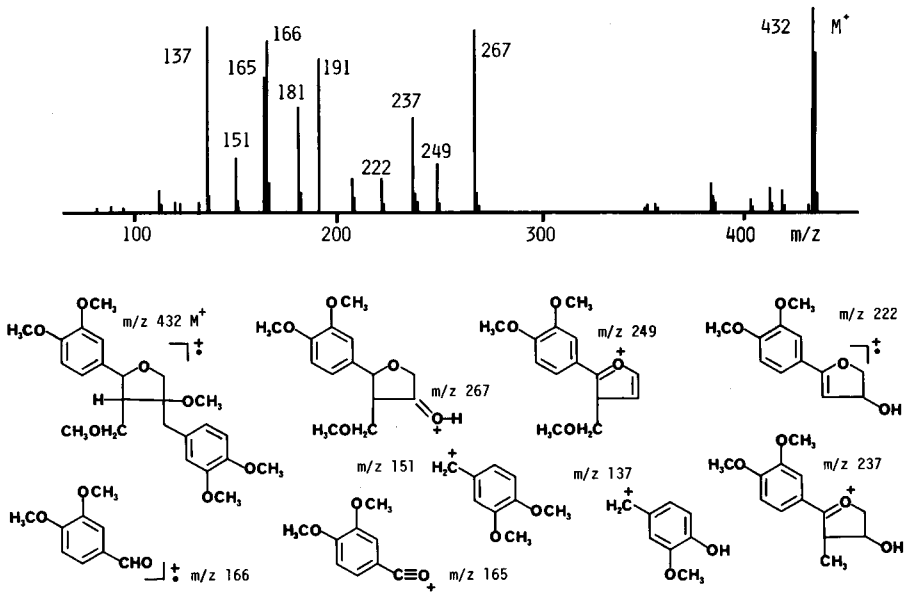

Fig. 2. Mass spectrum of SE-1 (olivil) tetramethyl ether (VI) and its main fragment ions.

absorption bands of ketone and aldehyde, and the index of hydrogen deficiency is one for the partial structure $C_6H_{10}O_3$. Pinkish red color reaction with diazotized sulfanilic acid (DSA) implyed the absence of benzyl alcohol group[2]. The doublet at δ 4.82 (J =7.5 Hz) is integrated as one proton (Fig. 1.) and could be attributed to the hydrogen on the benzyl carbon atom of the benzyl ether group judging from its chemical shift. Since this peak is AB doublet (J =7.2 Hz), the adjacent Cβ must substitute only one hydrogen. The singlet at δ 2.95 is equivalent to two protons corresponding to benzyl methylene group of α'-carbon atom. The adjacent β'-carbon atom must contain no protons because the signal of C α' at δ 2.95 is singlet. These spectral data suggest that the tertiary alcoholic hydroxyl group inevitably locates of the C β'. The multiplets in the region δ 4.5-4.2 were corresponding to four protons of two methylenes of γ and γ' carbon atoms. It presumes that one oxygen of the posturated ether linkage is alloted to a tetrahydrofuran ring which links Cα and Cγ' of two C_6C_3 units as a lignan. From these spectral data, the structure of the compound SE-1 is supposed to have the structure **III**. The structure **III** is same as that of olivil, of which structure was revised by M. SMITH.[3]

Fig. 2 shows the mass spectrum of SE-1 tetramethyl ether (VI) and its main fragmentation ions. The fragment ions of m/z 267, 237 and 222 support the above structure **III** indicating strongly that the tertiary alcoholic hydroxyl group locates at Cβ. The fragment ions of m/z 191, 181, 166, 165, and 151 are assigned to the fragments containing veratryl pendant groups. Table 2 shows high mass spectral data of SE-1 tetramethyl ether (VI).

The physical and chemical properties of SE-1 were all same as those of olivil reported[3,4] and of the authentic specimen given by Dr. D.C. AYRES except the specific rotation as

Table 2. High mass spectral data of olivil (SE-1) tetramethyl ether (VI)

OBSD.	CALCD. ERROR		FORMULA	INT.
m/z 432.2133	.2089	−1.4	$C_{24}H_{32}O_7$	31% M^+
267.1250	.1232	+1.8	$C_{14}H_{19}O_5$	26
237.1189	.1126	+1.3	$C_{13}H_{17}O_4$	27
224.1052	.1048	+0.3	$C_{12}H_{16}O_4$	26
222.0888	.0892	−0.3	$C_{12}H_{14}O_4$	30
208.1077	.1099	−2.2	$C_{12}H_{16}O_3$	33
206.0926	.0942	−1.6	$C_{12}H_{14}O_3$	34
191.1085	.1073	+1.3	$C_{12}H_{15}O_2$	35
190.0990	.0993	−0.2	$C_{12}H_{14}O_2$	27
181.0857	.0864	−0.6	$C_{10}H_{13}O_3$	41
179.0712	.0708	+0.4	$C_{10}H_{11}O_3$	40
166.0963	.0993	−2.9	$C_{10}H_{14}O_2$	50
165.0990	.0915	−1.4	$C_{10}H_{13}O_2$	49
147.0448	.0446	+0.2	$C_9H_7O_2$	40
138.0646	.0680	−3.4	$C_8H_{10}O_2$	46
137.0598	.0602	−0.4	$C_8H_9O_2$	55

Table 3. Specific rotations of the compound SE-1 and olivil

Compound	Specific rotation	Reference
SE-1	[α] D −37.5° (C=1.0, in acetone)	M. TERAZAWA *et al.*[1]
SE-1	[α] D −56.0° (C=0.5, in H_2O)	in this work
Olivil	[α] D −38.0° (C=0.5, in H_2O)	in this work
Olivil	[α] D −127.0° (in H_2O)	D. C. AYRES *et al.*[4]
Olivil	[α] D −35.5° (C=1.0, in MeOH)	G. KUDO *et al.*[15]

described in **2.2.**

SE-1 (III) was converted into cycloolivil (VIII) by the method reported.[4]

2.2 Specific rotation of the compound SE-1

The specific rotations of the compound SE-1 and olivil are shown in Table 3. Although the reported optical rotation of olivil is $[\alpha]_D$ −127° (in H_2O)[4], those of the

compound SE-1 and an authentic olivil given by Dr. AYRES are $[\alpha]_D$ −56.0° (c=0.5 in H_2O) and $[\alpha]_D$ −38.0° (c=0.5 in H_2O), respectively. The SE-1 has the specific rotation $[\alpha]_D$ −37.5° in acetone. The specific rotation is influenced by the solvent used.

3. Discussion

3.1 Olivil

Olivil was isolated from *Olea europeae* L. in 1833[5], but its structure was not determined for a long time until B.L. VANZETTI[6] offered the structure (IX) for it. The structure (IX) was used for olivil even after G. TRAVERSO[7] had proposed two possible revised structures (III) and (X) for it. Although K. FREUDENBERG and K. WEINGES[8] adopted the structure (X) for olivil, the structure (III) was finally established by M. SMITH[9] based on the NMR spectral data: from the ^{1}H-NMR spectral data of olivil dimethyl ether (V), a doublet at τ 5.25 (δ 4.75, J=7.5 Hz, in $CDCl_3$) was satisfied only by the structure (III).

As described in **2.1** in detail, the assignment of the doublet at δ 4.82 (J=7.5 Hz) of SE-1 (olivil) tetraacetate (IV) is the key point to elucidate its structure. The data on the mass fragmentation of SE-1 (olivil) tetramethyl ether (VI) support the structure **III** of olivil.

D.C. AYRES and S.E. MHASALKER[4] confirmed the revised structure of olivil as (I) from the behavior of optical rotatory dispersion of the diacetate of dimethyl-α-apocycloolivil (XI), which was derived from the olivil dimethyl ether (V). The structure of olivil as (III) is now widely accepted.

3.2 Specific rotation of SE-1

Specific rotations of the compound SE-1 and olivil are not exactly same even though they were measured in the same condition and are different from that of olivil reported[4]. Although the discrepancy in the specific rotations of the compound SE-1 and the authentic

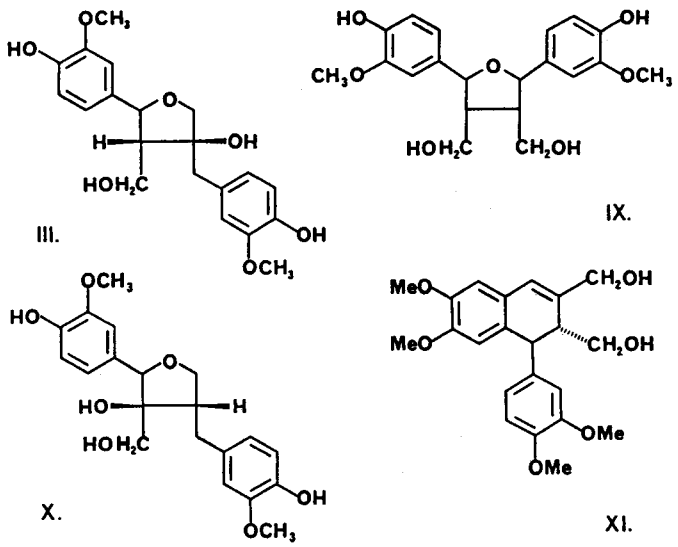

Chart B

olivil is not essential to their structures, it may rise a problm whether or not the co-occurrence of the optical isomer of olivil ((+)-olivil) reduces the levorotatory of the compound SE-1 ((−)-olivil).

The co-occurrence of optical active lignans ((+)-pinoresinol[13] and (−)-olivil) and optically inactive lignan ((±)-syringaresinol) in yachidamo[7] is very interesting.

3.3 Phenolic compounds in yachidamo

M. TERAZAWA *et al* have isolated many glycosides of coumarins[9], arylethanols[10], 4-hydroxycinnamyl alcohols[11], secoiridoids[12] and lignans[13] from the inner bark of yachidamo.

Since most of phenolic compounds occur generally as glycosides in the inner bark, the compound SE-1 found in the sapwood may also exist as glucoside in the inner bark of yachidamo. Olivil monoglucoside was isolated from the inner bark of *Ligstrum japonicum* THUNB. (Oleaceae) by KUDO *et al* recently[14].

As mentioned before, the compound SE-1 (olivil) was not detected in the heartwood extractives by PPC and TLC, it might have converted into some other compounds such as cycloolivil (VIII) during heartwood formation.

Yachidamo is known as one of trees which has wet heartwood in dark brown color[15]. The phenolic compounds in the sapwood might be involved in the discoloration of the wood during the heartwood fromation although the mechanism of the formation of wet heartwood is yet unknown.

4. Conclusion

The one of the three compounds isolated from the sapwood of yachidamo (*Fraxinus mandshurica* RUPR. var. *Japonica* MAXIM.) was identified to be olivil (III) by ^{1}H-NMR and MS spectroscopies.

Specific rotations of the compound SE-1 were $[\alpha]_D$ −37.5° (c=1.0 in acetone)[1], $[\alpha]_D$ −56.0° (c=0.5 in H_2O), although that of an authentic olivil was $[\alpha]_D$ −38.0° (c=0.5 in H_2O).

Since olivil was not detected in the heartwood extractives, in might have converted into the other compounds such as cycloolivil (VIII) during the heartwood fromation of the wood of yachidamo.

5. Experimental

5.1 Isolation of the compound SE-1 (olivil)

The compound SE-1 (olivil, III) was isolated as described in the previous paper[1] from the sapwood extractives of yachidamo (*Fraxinus mandshurica* RUPR. var. *japonica* MAXIM.).

The conditions for TLC: Wako-gel B-10, 250 μm thickness; developing solvents: SG-III: toluene, formic acid, ethyl formate/5: 1: 4 (v/v)[1]. The conditions for PPC: Toyo Roshi No. 51 (15x60 cm). Developing solvent: G-I: xylene: dimethylformamide/ 9: 1 v/v[1]. The conditions for HLC: Hitachi 635 HLC. Column: 8 x 500 mm, gel: Hitachi gel # 3011. Solvent: 95% EtOH, flow rate: 1.0 ml/min.

5.2 Physico-chemical properties of SE-1 and its derivatives

The instruments used for analyses were same as those described in the other papers[1,9-13] except a JMS-01SG-02 for high MS and a Hitachi R-24 for 90 MHz NMR spectroscopies. Melting points were not corrected.

5.2.1 SE-1 (olivil, III): Mp 112-114°C (recrystallized from 96% EtOH, Ref[4]. 118-120 °C from MeOH), 136-138°C (recrystallized from H_2O, lost crystalline water during 80-100° C). TLC (SG-III) R_f 0.22. PPC (G-I) R_f 0.14. $[\alpha]_D$ −37.5° (c=1.0 in acetone), $[\alpha]_D$ −56.0° (c=0.5 in H_2O). [An authentic olivil $[\alpha]_D$ −38.0° (c=0.5 in H_2O)]. Pinkish red with DSA. *Anal. Calcd.* for $C_{20}H_{24}O_7$: C, 63.83; H, 7.16 and for $C_{20}H_{24}O_7$. EtOH: C, 62.54; H, 7.16. *Found*: C, 62.50; H, 7.10 (the sample recrystallized from ethanol). MS *m/z*: 376.1534 (M^+, int. 40%), *Calcd.* for $C_{20}H_{24}O_7$ M=376.1522, measured by a JMS-01SG-2. Other fragments: see Table 1. UV λ_{max}^{EtOH} nm (log ε): 232 (3.28), 282 (2.85); $\lambda_{max}^{EtOH-0.1NNaOH}$ nm (log ε): 354 (3.40), 296 (2.95). IR ν_{max}^{KBr} cm^{-1}: 3380, 3360 (OH), 2950-2850 (CH), 3080, 3020, 1620, 1610, 1510 (Ph), 1470, 1440. ^{1}H-NMR (10% in d_6-DMSO, 60 MHz) δ ppm: 8.62 (*s.*, 1H ph-OH), 8.49 (*s.*, 1H ph-OH), 7.02-6.50 (*m.*, 6H, aromatic), 4.60 (*d.*, *J*= 6.5 Hz, 1H, overlapped partially by signal of OH at 4.53), 4.35 (*m.*, 2H. $-CH_2-$), 3.60 (*t.*, *J*= 6.3 Hz, 2H, methylene proton of ethanol as solvent of crystallization), 3.65-3.20 (*m.*, $-CH_2-$ and β-methine protons), 3.72 (*s.*, 6H, two Ar-OCH_3), 2.79 (*s.*, 2H, α'-methylene protons), 2.49 (*m.*, CD_2HSOCD_3), 1.05 (*t.*, *J*=6.3 Hz, 3H, methyl proton of ethanol as solvent of crystallization). This spectrum was changed by dilution with two drops of D_2O as follows: 7.15-6.60 (*m.*, 6H, aromatic), 4.64 (*d.*, *J*=7.2 Hz, 1H, α-proton), 3.75-3.30 (*m.*, 5H, overlapping of $-CH_2-$ of ethanol, *J*=6.3 Hz, $-CH_2-$, and β-methine protons), 2.85 (*s.*, 2H, α'-protons), 2.60 (*m.*, CD_2HSOCD_3), and 1.10 (*t.*, 3H of ethanol, *J*=5.3 Hz).

5.2.2 SE-1 tetraacetate (IV): olivil (III) was treated with pyridine and acetic anhydride at 55±2°C for 8 hr and a tetraacetate was obtained as amorphous, but pure on TLC, R_f 0.43 (SG-III). *Anal. Calcd.* for $C_{28}H_{32}O_{11}$: C, 61.31; H, 5.84. *Found*: C, 61.42; H, 5.93. IR ν_{max}^{KBr} cm^{-1}: 1760, 1730. ^{1}H-NMR (40mg in 0.5 ml $CDCl_3$) δ ppm: 7.15-6.58 (*m.*, 6H, aromatic), 4.82 (*d.*, *J*=7.27 Hz 1H, α-methine), 4.56-4.34 (*m.*, 2H, γ-methylene), 4.2-3.9 (*m.*, 2H, γ'-methylene), 3.82 (*s.*, 3H, ArOCH_3). 3.78 (*s.*, 3H, ArOCH_3), 2.96 (*s.*, 2H, α'-methylene), 2.29 (*s.*, 6H, two ArOCOCH_3), 2.05 (*s.*, 3H, primary alc-COCH_3), 1.80 (*s.*, 3H, tertiary alc-COCH_3). MS *m/z*: 544 (M^+), 502 (M^+-42), 484 ($M^+-42-18$), 442 ($M^+-42x2-18x2$), 332 ($M^+-42x2-18x3$), 246, 222, 1888, 150, 136.

5.2.3 SE-1 dimethyl ether (V): olivil(III) was treated with CH_2N_2. The crude methyl ether was purified by HLC. Mp 154-155°C (Ref[4]. 156°C). *Anal. Calcd.* for $C_{22}H_{28}O_9$: C, 65.33; H, 6.98. *Found*: C. 65.37; H, 7.80. MS *m/z*: 404. 1855 (M^+, int. 10%, *Calcd.* 404. 1835). MS *m/z*: 404 (M^+), 386, 355, 253,239, 235, 223, 194 177, 167, 165, 151, 137. ^{1}H-NMR (40mg in d_6-DMSO) δ ppm: 7.20-6.79 (*m.*, 6H, aromatic), 4.75 (*d.*, *J*=7.2 Hz, 1H, α-methine), 3.9-3.4, (*m.*, 4H, γ-and γ'-methylenes), 2.30 (*m.*,1H, α-methine), 2.0 (m., CD_2HSOCD_3), 3.5 (OH). Peak of hydroxyl group at δ 3.5 and 2.72 disappeared by D_2O dilution and multiplet at δ 2.98 changed to a doublet at δ 3.0 (*J*=7.2 Hz). The other signals were not changed.

5.2.4 SE-1 tetramethyl ether (VI): Olivil (III) was treated with dimethyl sulfate and potassium hydroxide aq. Mp 143-146°C. *Anal. Calcd.* for $C_{24}H_{32}O_{11}$: C, 66.6; H, 7.46. *Found*: C, 65.93; H, 7.62. MS *m/z*: 432.2133 (M^+, int. 31%, *Calcd.* as $C_{24}H_{32}O_{11}$ M= 432.2089). The other fragments: see Table 2. ^{1}H-NMR(40mg in 0.5 ml d_6-acetone, 90

MHz, by a Hitachi R-22) δ ppm: 6.85-6.50 (*m.*, 6H, aromatic), 4.42 (*d.*, $J=7.2$ Hz, 1H, α-methine), 3.6-3.1 (*m.*, 4H, γ-and γ'-methylenes and 12H, four ArOCH_3), 2.68 (*m.*, 2H, α'-methylece), 2.95 (*m.*, β-methine), 1.7 (*m.*, CD_2HSOCD_3).

5.2.5 Cycloolivil dimethyl ether (VIII): Olivil demethylether (V) was treated with boron trifluoride etherate and sodium borohydride by the same method reported by D.C. AYRES[4] and a compound was obtained. 181-182°C (Ref[4]. MP 180-181°C). *Anal. Calcd.* for $C_{26}H_{32}O_{11}$: C, 65.99; H, 6.04. *Found*: C, 65.87, H, 6.11. IR ν_{max}^{KBr} cm^{-1}: 3300, 3200 (OH), 2850-2950 (CH), 1605, 1590, 1510, (Ph), 1465, 1450, 1415, 1400, 1350, 1315, 1300, 1260, 1250, 1230, 1210, 1190, 1150, 1140, 1120, 1110, 1095, 1080, 1030, 1020, 985, 950, 925, 870, 855.

5.2.6 Permanganate oxidation of SE-1 dimethyl ether: Veratric acid (VII): Olivil dimethyl ether (V) was treated with potassium permanganate and sodium hydroxide aq., and then degradation product was extracted with diethyl ether after acidification with dil. H_2SO_4. Veratric acid (VII) was obtained as colorless crystals. Mp 195-197°C. *Anal. Calcd.* for $C_9H_{10}O_{10}$ (M=200): C, 59.33; H, 5.33. *Found*: C, 59.40; H, 5.28. TLC: R_f 0.82 (SG-III).

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References

1) TERAZAWA, M. and SASAYA, T.: *Mokuzai Gakkaishi*, **17**, 167 (1971)
2) SANO, Y. and SAKAKIBARA, A.: *ibid.*, **16**, 121 (1970)
3) SMITH, M.: *Tetrahedron Lett.*, 991 (1963)
4) AYRES, D. C. and MHASALKER, S. E.: *J. C. S., 3586 (1965)*
5) PELLETIER, Y.: *Ann. Chim. Phys.*, **51**, 196 (1833)
6) VANZETTI, B. L.: *Acad. d'Italia, Mem Classa Sci.*, **13**, 411 (1937)
7) TRAVERSO, G.: *Gazz, Chim. Ital.*, 88, 851 (1958): **90**, 792 (1960)
8) FREUDENBERG, K. and WEINGES, K. *Tetrahedron Lett.*, 1077(1962)
9) TERAZAWA, M. and SASAYA, T.: *Mokuzai Gakkaishi*, **16**, 192 (1970).
10) TERAZAWA. M., OKUYAMA, H. and MIYAKE, M.: *Proc. Hokkaido Br. J. Wood Res. Soc.* (in Japanese), **5**, 32 (1973).
11) TERAZAWA, M., OKUYAMA, H. and MIYAKE, M.: *Mokuzai Gakkaishi*, **30**, 409 (1984).
12) TERAZAWA, M.: *Res. Bull. Coll. Exp. Forests. Fac. Agre., Hokkaiko Univ.*, **43**, 109 (1986)
13) TERAZAWA, M.: *J. Fac. Agri., Hokkaido Univ.*, **62**, (1986)
14) KUDO, G., NOHARA, T., KOMORI, T., KAWASAKI, T. and SCHOLTOEN, H.-R.: *Plant medica*, **40**, 250 (1980).
15) YAZAWA, K., ISHIDA, S. and MIYAJIMA, H.: *Mokuzai Gakkaishi*, **11**, 71 (1965)

要　　約

ヤチダモ（*Fraxinus mandshurica* RUPR. var. *japoniica* MAXIM）の辺材から単離された3種のフェノール成分 SE-1, SE-2, SE-3 のうち，後者2種は，それぞれ(±)-syringaresinol（I）と fraxinol（II）と同定されていた。しかし，SE-1は未同定のままであった。本報告は，SE-1の構造について，NMR，MS，分解反応などによる構造解明を取扱っている。

化合物 SE-1は，そのハイマスにより得られた分子イオンピーク m/z 376.2534 から，分子式 $C_{20}H_{24}O_7$ が推定された（Table 1）。エタノールから再結晶させた SE-1は，結晶溶媒としてエタノールを1モル含むことが^{1}H-NMR スペクトルにより明らかになり，元素分析値の理論値との相違が明らかになった。

SE-1は ピリジン・無水酢酸中，室温では完全にアセチル化されないが[1]，55± 2°C では唯一のテストラアセテート（IV）を与える。このアセテート（IV）の^{1}H-NMR スペクトルにおける δ 1.80 のシングレットは，第3級アルコール性アセトキシル基のメチルプロトンに由来するものである（Fig. 1）。SE-1（III）のマススペクトル中の m/z 137 のフラグメントイオン（Table 1）は，ハイドロキシメトキシベジルカチオンに相当し，そのアセテートの^{1}H-NMR スペクトルの結果とあわせ，2個のグアィアシル核をペンダントグループとして有することが推定された。このことは，SE-1のジメチルエーテル（IV）を KM_nO_4 酸化することによりベラトルム酸（VII）を得ることからも支持された。SE-1の分子式 $C_{20}H_{24}O_7$ から，2個のグアイアシル核 $C_{14}H_{14}O_4$ を差し引いて残る $C_{16}H_{10}O_3$ の部分構造中の3個の酸素のうち，2個はアルコール性水酸基によるものであることが^{1}H-NMR スペクトルから明らかである（Fig. 1）。

他の1個の酸素は，IR スペクトルにおいて SE-1が，アルデヒド，ケトン，エステルの吸収を示さないことおよび，水素不足指数の検討から，エーテル結合に関与しているものと推定される。2個あるベンジル部分構造のうち，1個はベンジルメチレンの吸収を示し，そのシグナルがシングレットであることから隣接炭素は3級炭素であることを示す。他の1個は，ベルジルエーテルのベンジルメチンの吸収を示し，そのシグナルが AB ダブレットであることから隣接炭素にプロトンが1個存在することが明らかである。SE-1の基本構造をリグナンとすると，推定されるエーテル結合は，α および γ' 炭素を結合したテトラヒドフラン環中のものと考えるのが最も自然である。以上，NMR，MS スペクトルのデータの解析により，SE-1は構造IIIを有すると推定した。この構造IIIは，M. Smith によって訂正された Olivil の構造に等しい。

SE-1テトラメチルエーテル（VI）のマススペクトルおよびそのフラグメンテーションは SE-1が第三級のアルコール性水酸基が β' 位にあることを示し，構造IVを有することを支持する（Fig 2. Table 2）。

SE-1の物理化学的諸性質を Olivil のそれらと比較した結果，SE-1を Olivil と同定した。但し，比旋光度は Olivil の文献記載のものと異なっていることが明らかとなった（Teble 3）。

SE-1 (Olivil) は，辺材に特有の成分であり，心材抽出物中に，TLC, PPC 等による分析では検出しえなかった。ヤチダモは，暗褐色の心材を有しており，多湿心材としても知られている。辺材中の SE-1 は，心材形成時に他の成分に変換すると推定される。