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Author(s)	SASAYA, Takashi; 笹谷, 宜志
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Diarylheptanoids of *Alnus hirsuta* TURCZ. (*Betulaceae*)[*1,2]

By

Takashi SASAYA[*3]

ケヤマハンノキのジアリルヘプタノイド

笹谷 宜志

CONTENTS

1. Introduction

In the course of the investigation of the extractives of keyamahan-no-ki *Alnus hirsuta*, ten phenolic compounds were isolated from the ethanol extracts of the wood. Five of them had already been reported to date and they were identified with three diarylheptanoids [1, 7-di-(*p*-hydroxyphenyl)-heptan-3, 5-diol I (E-3), 1, 7-di-(*p*-hydroxyphenyl)-heptan-3-one-5-ol II (E-4), trideoxyasadanin-8-ene XIII (E-1)], β-guaiacylethyl ferulate XVIII (E-2) and vanillic acid, respectively.

In further scrutiny of the extractives from the same source, four phenolic compounds had further been isolated. One of them (E-9) was diarylheptanoid with an acyclic structure, and other two compounds (E-5 and -7) had a cyclic carbon

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[*2] Presented in part at the 33rd Annual Meeting of the Japan Wood Research Society at Kyoto, March-April 1983 and at the 1983 International Symposium on Wood and Pulp Chemistry, at Tsukuba, May 1983.

[*3] Laboratory of Wood Chemistry, Dept. of Forest Products, Fac. of Agriculture, Hokkaido University.
北海道林学農学部林産学科　木材化学講座

skeleton. The residual compound (E-6) was related to diarylheptanoid.

In this paper, it is described the chemical structure for these four compounds. Also, the chemical features of diarylheptanoids in *Betulaceae* had briefly been discussed.

2. Experimental

All chromatographic and spectroscopic procedures in this work were succeeded in accordance with previous paper1). Also, melting points were not corrected. The materials in each fraction were monitored by TLC with the solvent system of toluene : ethyl formate : formic acid (5 : 4 : 1) as mobile phase. ^{1}H-NMR spectra obtained with JNM-FX 200 FT NMR spectrometer. The following abbreviations were used for the presentation of NMR data : d=doublet, m=multiplet, s=singlet and t=triplet. Acetylation of compounds E-5, -7 and -9 were usually carried out with acetic anhydride and dry pyridine.

2.1. Isolation of Compound III (E-9)

The 5% KOH soluble fraction (ca. 5 g) was chromatographed on a silica gel column (3.8×70.0 cm) using benzene : acetone (20 : 1-5 : 1) as elution solvent, and fractions of 950×30 mℓ (No. 1-950) were obtained. Fractions No. 773-812 were combined and concentrated. A crude material obtained was purified with benzene : acetone (1 : 1) to give a colorless oily state substance (12 mg).

Compound E-9 was positive to diazotized sulfanillic acid (DSA) and ferric chloride, and was negative to 2, 4-dinitrophenylhydrazine (2, 4-DNPH) and quinonemonochlorimide (QMCI), respectively. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm : 225, 280, UV $\lambda_{\max}^{\mathrm{EtOH-0.1NNaOH}}$ nm : 235, 287, 302. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} : 3383, 3183, 1608, 1600, 1507, 1450, 1285, 1230, 1090, 910, 815. MS m/z: 300.1724 (M$^+$), 282 (M-18), 133, 120, 107 (base ion). *Anal. Calcd.* for $C_{19}H_{24}O_3$: C 76.00, H 8.00%. *Found*: C 75.92, H 7.90%.

By acetylation, E-9 (10 mg) gave triacetate (10 mg, oily). $[\alpha]_D^{21}=+6.10°$ (c=1.23 in MeOH). ^{1}H-NMR (1.43% in $CDCl_3$) δ : 1.30-1.90 (8H, m), 2.00 (3H, s), 2.25 (6H, s), 2.45-2.80 (4H, m), 4.80-5.00 (1H, m), 6.96 (2H, d, J=8 Hz), 7.15 (2H, d, J=8 Hz).

2.2. Isolation of Compound XVII (E-6)

Fractions No. 5-41 was collected and evaporated. A crude solid was recrystallized with benzene to give a pale yellowish needles (140 mg). m. p. 203-206°C. It gave positive color test to DSA, ferric chloride and 2, 4-DNPH, and was negative to QMCI. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm : 206, 346, UV $\lambda_{\max}^{\mathrm{EtOH-0.1NNaOH}}$ nm : 273, 422. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1} : 3260, 2960, 1640, 1580, 1500, 1200, 975, 870, 830, 810. MS m/z : 292.1098 (M$^+$, base ion), 264 (M-CO), 186, 144, 115. ^{1}H-NMR (0.9% in 1, 4-dioxane-d_8) δ : 2.47 (1H, broad s), 2.61 (2H, m), 2.99 (2H, t, J=6 Hz), 5.98-6.02 (2H, m), 2.61 (2H, s, d, J=10 Hz, overlapped), 6.42 (1H, d, J=10 Hz), 6.21 (1H, d, J=8 Hz), 6.81 (1H, d, J=8 Hz), 7.06 (2H, d, J=8 Hz), 7.23 (2H, d, J=8 Hz). *Anal. Calcd.* for $C_{19}H_{16}O_3$: C 78.08, H 5.48%. *Found*: C 78.06, H 5.52%.

E-6 (10 mg) and anhydrous sodium aetate (20 mg) in 1 mℓ of acetic anhydride were heated on a water bath at 80°C for one hour. The raction product was poured into ice water and the resulting precipitate was collected. Purification with 50% EtOH gave monoacetate of colorless plates (11 mg), m. p. 120°C. IR ν_{max}^{KBr} cm^{-1}: 1760, 1655, 1590, 1500, 1365, 1210. MS m/z: 334 (M$^+$), 292 (M-42, base ion), 264, 186, 144, 115. ^{1}H-NMR (1.42% in $CDCl_3$) δ: 2.40 (3H, s), 2.66 (2H, m), 3.05 (2H, t, J=6 Hz). 6.02-6.10 (2H, m), 6.44 (1H, m), 6.82-6.83 (1H, m), 7.00-7.09 (3H, m), 7.19-7.26 (1H, m). *Anal. Calcd.* for $C_{21}H_{18}O_4$: C 75.43, H 7.43%. *Found*: C 75.24, H 5.58%.

2. 3. Isolation of Compound XI (E-5)

In the previous paper[1], it has been mentioned that compounds XIII (E-1) and XVIII (E-2) were isolated from the 10% sodium carbonate soluble fraction using cellolose column chromatography. After the separation of these compounds, the residual solution was concentrated to give a syrup (ca. 5 g). The syrup was chromatographed on a silica gel column (3.8×70.7 cm), eluting with benzene : acetone (20 : 1-5 : 1) as elution solvent, and then 850×30 mℓ of fractions were obtained. Fractions No. 340-600 were combined and a crude material was obtained after the removal of the solvent. Several recrstallization with 70% EtOH gave a colorless needles (ca. 100 mg, E-5), m. p.>300°C. E-5 was positive to DAS and ferric chloride, and was negative to 2, 4-DNPH and QMCI, respectively. UV λ_{max}^{EtOH} nm: 255, 260, 303. UV $\lambda_{max}^{EtOH-0.1NNaOH}$ nm: 262, 305, 334. IR ν_{max}^{KBr} cm^{-1}: 3420, 3140, 1610, 1580, 1500, 1435, 1435, 1405, 1370, 1230, 930, 800. MS m/z: 314 (M$^+$), 296 (M-18), 278 (M-36), 260, 255, 225, 211 (base ion), 197, 183, 165. *Anal. Calcd.* for $C_{19}H_{22}O_4$: C 72.59, H 7.05%. *Found*: C 72.96, H 7.08%. Acetylation of E-5 (10 mg) gave an amorphous tetraacetate (11 mg). ^{1}H-NMR (0.9% in $CDCl_3$) δ: 1.85-1.97 (6H, m), 2.01 (6H, s), 2.44 (6H, s), 2.57-2.75 (4H, m), 4.95 (2H, m), 7.11-7.28 (6H, m).

2. 4. Isolation of Compound XII (E-7)

Eluate No. 74-205 from the same column was combined, and then the solvent was removed to give a crude solid which gave a colorless needles after several recrystallization with benzene : acetone (1 : 1) (ca. 300 mg, E-7), m. p. 190-192°C. E-7 was positive to DSA, ferric chloride and 2, 4-DNPH, and was negative to QMCI. UV λ_{max}^{EtOH} nm: 253, 303. UV $\lambda_{max}^{EtOH-0.1NNaOH}$ nm: 263, 332. IR ν_{max}^{KBr} cm^{-1}: 3400, 3120, 1700, 1610, 1580, 1500, 1410, 1250, 1095, 810. MS m/z: 312.1395 (M$^+$), 294 (M-18), 225, 221 (base ion), 197, 183, 165. *Anal. Calcd.* for $C_{19}H_{20}O_4$: C 73.16, H 6.45%. *Found*: C 73.95, H 6.59%.

Acetylation of E-7 (10 mg) gave an amorphous triacetate (8 mg). ^{1}H-NMR (0.52% in $CDCl_3$) δ: 1.97-2.11 (2H, m), 2.17 (3H, s), 2.20 (6H, s), 2.68-3.15 (8H, m), 4.80 (1H, m), 6.96-7.26 (6H, m).

3. Results and Discussion

Four compounds E-5, -6, -7 and -9 were isolated from the acidic fraction of the ether solubles. It had already been reported that phenolics obtained from wood of *A. hirsuta* could be classified into three groups (A. B and C) considering the features of their chemical properties and the results of UV and MS spectra[1].

The physicochemical properties of the newly isolated four compounds (E-5, -6, -7 and -9) were shown in Table 1 together with those of the previously isolated four compounds (E-1, -2, -3 and -4).

Table 1. Physicochemical properties of the Extractives of *Alnus hirsuta*

	E-1 (XIII)	E-2 (XVIII)	E-3 (I)	E-4 (II)	E-5 (XI)	E-6 (XVIII)	E-7 (XII)	E-9 (III)
Melting point °C	238-341	194-195	165-166	131-132	>300	203-206	190-102	oily
Color reaction								
FeCl$_3$	+	+	+	+	+	+	+	+
diazotized sulfanillic acid	+	+	+	+	+	+	+	+
2, 4-dinitrophenylhydrazine	+	+	−	+	−	+	+	−
quinonemonochlorimide	−	−	−	−	−	−	−	−
UV spectrum								
λ_{max} nm	297	329	279.5	280	303	346	303	280
IR spectrum								
$\nu_{C=O}$ cm^{-1}	1675	1700		1690		1640	1700	
Mass spectrum								
M+ m/z	294	344	316	314	314	292	312	300
base ion m/z	211	137	107	107	211	292	211	107
Molecular formula	$C_{19}H_{18}O_3$	$C_{19}H_{20}O_6$	$C_{19}H_{24}O_4$	$C_{19}H_{22}O_4$	$C_{19}H_{22}O_4$	$C_{19}H_{16}O_3$	$C_{19}H_{20}O_4$	$C_{19}H_{24}O_3$
Group	B	C	A	A	B	C	B	A

+ : positive, − : negative

3. 1. 1, 7-di-(*p*-hydroxyphenyl)-heptan-3-ol III (E-9)

Compound E-9 is positive to ferric chloride and DSA, and is negative to 2, 4-DNPH and QMCI, respectively. The formula $C_{19}H_{24}O_3$ for this compound (M^+ : m/z 300.1724) is given by the results of the high resolution mass spectrum and the elemental analysis. The ion peak at m/z 107 is assigned to $\cdot CH_2\text{-}Ar(OH)$ which is characteristic of an acyclic structure for diarylheptanoid such as hannokinol I and hannokinin II. Other rmarkable peaks at m/z 133 and 120 are originated from the ions of $CH_3\text{-}CH{=}CH\text{-}Ar(OH)\rceil^+$ and $CH_2{=}CH\text{-}Ar(OH)\rceil^+$, respectively. (Fig. 1).

Acetylation of E-9 gave triacetate, $[\alpha]_D^{21} = +6.10°$. Two singlets at δ 2.00 and 2.27 in the ^{1}H-NMR spectrum show the presence of an alcoholic and two phenolic acetoxyl groups (Fig. 2). Also, two doublets at δ 6.96 and 7.15 are derived from two *p*-hydroxyphenyl groups (AA′BB′ system) and the multiplet at 1.30-1.90 region correponds to four methylene groups on the side chain. On the other hand, the multiplet at δ 2.45-2.80 is due to four benzylic protons and the complicated signal at δ 4.99 is assigned to a proton at C_3 position on the side chain.

The results of color reactions and spectroscopies support that E-9 is to be 1, 7-di-(*p*-hydroxyphenyl)-heptan-3-ol III and could be classified into group A.

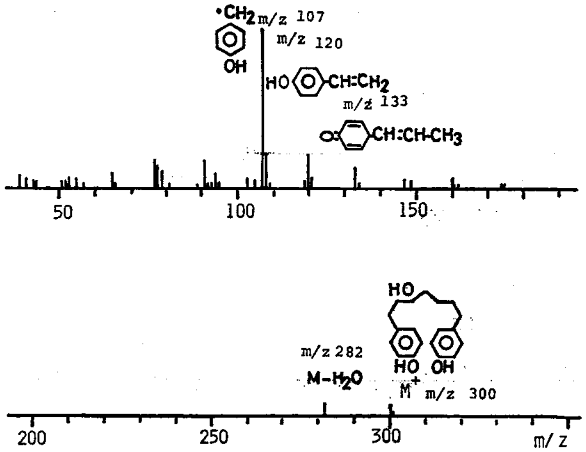


Fig. 1. Mass spectrum of E-9.

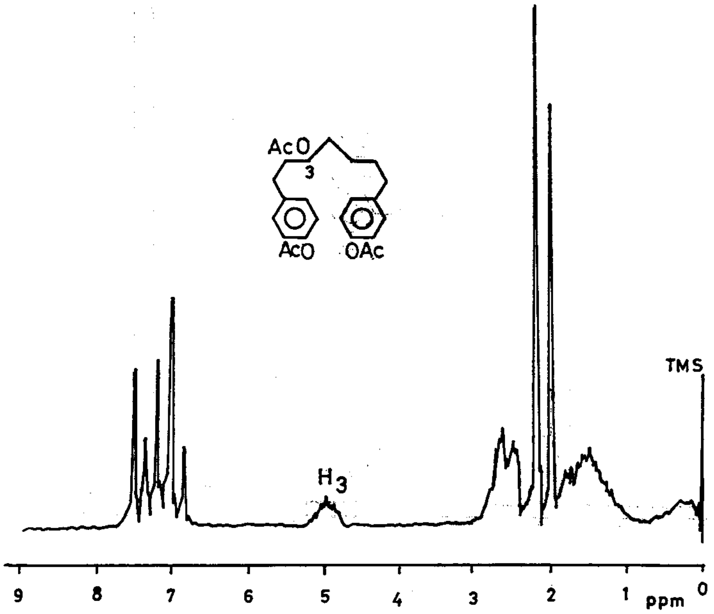


Fig. 2. ^{1}H-NMR spectrum of E-9 triacetate.

Earlier, this compound has been isolated from the heartwood of *Centrolobium robstum* and *C. tomentosum* (*Legminosae*) designated as (+)-centrolobol which the optical rotation of its triacetate was $[\alpha]_{D}^{25}=+8.3^{\circ}$[2].

3.2. Compound XI (E-5) and XII (E-7)

Compound E-5 which is classified into group B is negative to 2, 4-DNPH and QMCI reactions. The formula $C_{19}H_{22}O_4$ for E-5 (M^+ : m/z 314) has been determined by the results of the elemental analysis and mass spectrum. In the mass spectrum, the prominent ion peak exhibits at m/z 211 (base ion) due to a biphenyl moiety as the partial structure established in the case of compound E-1[1]. Two characteristic ion peaks at m/z 296 and 278 correspond to the M-18 and M-36 fragment ion peaks by release of water, respectively. (Fig. 3). Other fragmentation pattern is very similar to that of compound E-1.

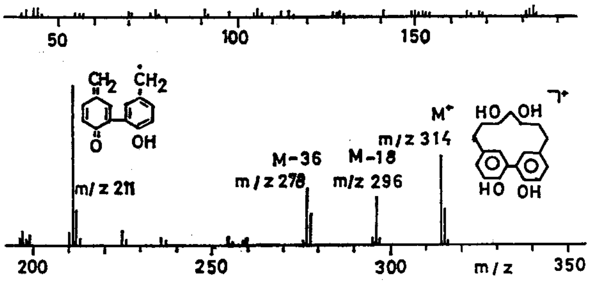


Fig. 3. Mass spectrum of E-5.

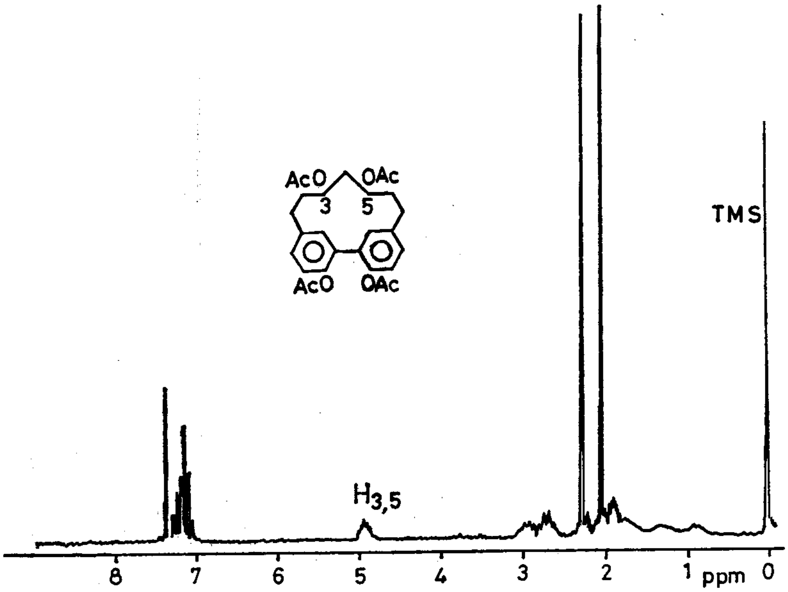


Fig. 4. ^{1}H-NMR spectrum of E-5 tetraacetate.

Two singlets at δ 2.01 and 2.24 in the ^{1}H-NMR spectrum of E-5 tetraacetate indicate the presence of two alcoholic and two pehnolic hydroxyl groups in the structure. The multiplet at δ 4.95 is attributable to protons at C_3 and C_5. Also, two multiplets at δ 1.85-1.97 and 2.57-2.75 are assigned to three methylene groups on the side chain and four benzylic protons, respectively. Furthermore, the color test with QMCI indicates non-hydroxylation at the benzylic position. These findings support that E-5 has the structure XI.

E-7 is positive to 2, 4-DNPH and is negative to QMCI, respectively. This indicates the existence of a carbonyl group in that structure which is further supported by adsorption band at 1700 cm^{-1} in the IR spectrum. On the other hand, the color reaction with QMCI indicates that this compound is not hydroxylation at benzylic position such as E-5. The formula $C_{19}H_{20}H_4$ for E-7 (M^+ : m/z 312.1395) is given by the results of the high resolution mass spectrum and the elemental analysis. The conspicuous ion peaks at m/z 294 and 211 (base ion) are originated from M-18 and a biphenyl moiety, respectively. The features of other fragment ion peaks agreed very closely with that of E-5 (Fig. 5).

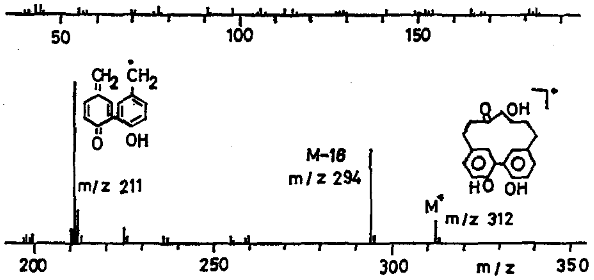


Fig. 5. Mass spectrum of E-7.

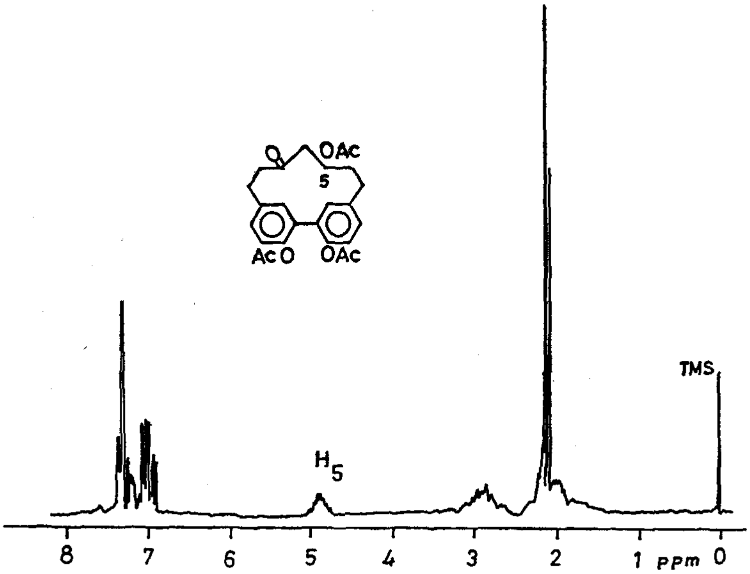


Fig. 6. ^1H-NMR spectrum of E-7 triacetate.

Two singlets at δ 2.17 and 2.20 in the ^1H-NMR spectrum of E-7 triacetate are due to an alcoholic and two phenolic acetoxyl groups. Furthermore, the multiplet at δ 4.80 is shown to arise from a proton at C_5 position on the side chain. (Fig. 6). It is supported from the results of color reactions and spectroscopies that E-7 has the structure XII and is classified into group B.

The physicochemical features of those two compounds E-5 and E-7 coincide evidently with those of alnusdiol and alnusonol from the wood of *A. japonica*[3,4].

3.3. Compound XVII (E-6)

Compound E-6 (M^+ : 292.1098 ; group C) has the formula $C_{19}H_{16}O_3$, which is determined by the results of the high resolution mass spectrum and the elemantal analysis. Also, this compound is positive to 2, 4-DNPH, and is negative to QMCI, respectively. On the other hand, the absorption maxima in the UV and IR spectra of E-6 reveal at 346 nm and 1640 cm^{-1}. This facts suggest the occurrence of conjugated carbonyl group and the lack of hydroxylation at benzyl position in that structure. Moreover, an absorption band at 810 cm^{-1} indicates that E-6 has a 1, 4-substituted phenyl moiety as the partial structure.

The mass spectrum of this compound exhibits the parent ion peak at m/z 292 which also is a base ion peak. The prominent ion peak at m/z 186 may be caused by release of carbonyl group from M$^+$, followed by elimination of a fragment of m/z 78 ($C_6H_5 \cdot + H$). On the other hand, the ion peak at m/z 144 is derived from the ion peak at m/z 264 (M-CO) which involves fission of m/z 117 fragment by RDA. Furthermore, the ion peak at m/z 115 arises from the ion m/z 264 by elimination of a fragment m/z 121, followed by release of m/z 26 fragment. (Fig. 7).

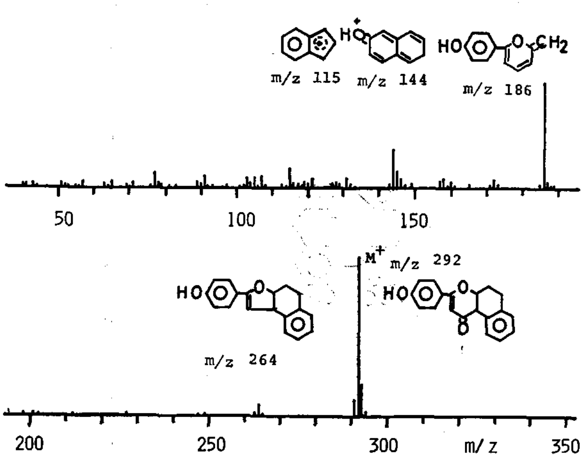


Fig. 7. Mass spectrum of E-6.

The ^{1}H-NMR spectrum of E-6 in 1, 4-dioxane-d_8 shows a complicated signal at δ 2.47 and a triplet at δ 2.61 (J=6 Hz) which are caused by two methylene groups at C_7 and C_8 positions. The conspicuous singlet at δ 6.12 overlapping the ion peak of phenyl proton is attributed to a proton at C_3 position. Other two doublets at δ 7.06 (J=8 Hz) and 7.23 (J=8 Hz) are originated from the protons of B-ring ($H_{3',5'}$ and $H_{2',6'}$: AA′BB′ system). The multiplet at δ 5.89-6.02 in downfield may be due to the protons at C_5 and C_6 positions. The doublets at δ 6.61 (J=ca. 8 Hz) and 6.81 (J=ca. 8 Hz) resulting from ortho coupling to each other may presumably be arised from the protons on tetrahydronaphthalene moiety. (Fig. 8).

By acetylattion of E-6 gave monoacetate. The molecular ion peak in the mass spectrum of this acetate appeared at m/z 334 and the base ion peak at m/z 292 (M-42). The later may be formed by elimination of an acetyl group from M$^+$. In the ^{1}H-NMR spectrum of E-6 monoacetate, the singlet at δ 2.40 corresponds to a phenolic acetoxyl group. Two multiplets at δ 2.62-2.80 and 2.97-3.05 are assigned

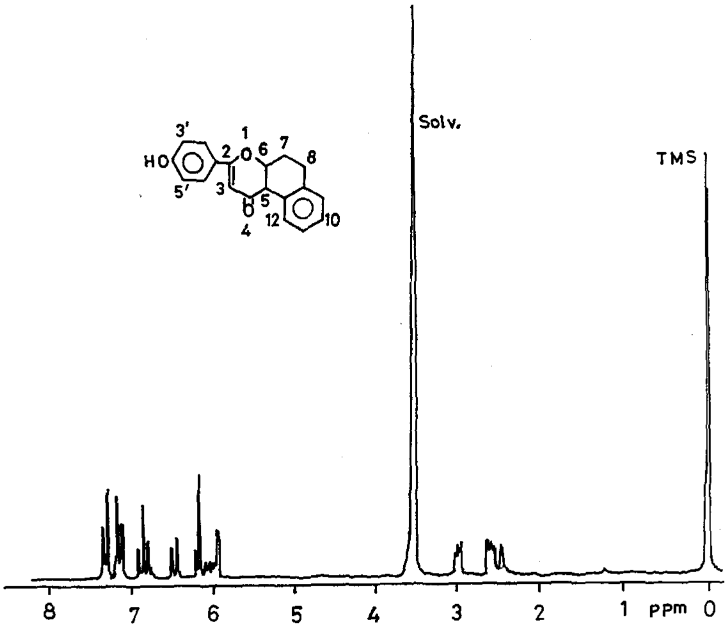


Fig. 8. ^{1}H-NMR spectrum of E-6 in 1, 4-dioxane-d_8.

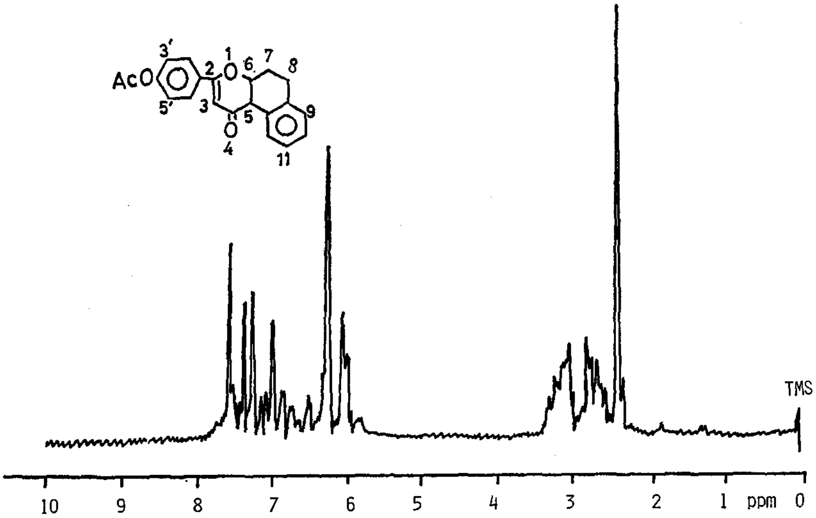


Fig. 9. ^{1}H-NMR spectrum of E-6 monoacetate.

to methylene groups (H_7 and H_8). (Fig. 9).

These findings of the color reactions and physicochemical properties support that E-6 has the structure XVII. This compound has a tetrahydronaphthoflavone structure as a basic carbon skeleton and has not been reported as yet. Considering the biogenesis of 9 phenylperinaphthenone proposed by EDWARDS *et al.*[5], compound E-6 may also be formed by elimination of an actate carbonyl group from two cinnamate units and an acetate unit during biosynthesis.

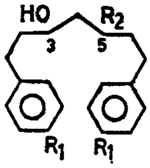
Table 2. Diarylheptanoids and related compounds in *Betulaceae*

		Group A										Group B						Group C		
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
Betuleae																				
Alnus																				
A. hirsuta	wood	X	X	X								X	X	X				X	X	
	green bark				X	X														
A. japonica	wood	X	X					X				X	X		X	X				
A. rubra	wood						X													
A. fruticosa	leaves								X											
A. mandshurica	leaves								X											
A. firma	buds									X	X									X
Betula																				
B. platyphylla	green bark		X																	
Coryleae																				
Ostrya																				
O. japonica	wood													X			X			
Carpinus																				
C. laxiflora	wood													X						
C. japonica	wood													X*						
C. tschonoskii	wood													X*						

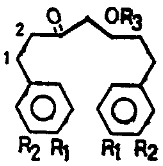
X: isolated, *: detected on TLC

All of compounds III, XI, XII and XVII obtained from the wood of *A. hirsuta* are diarylheptanoids with C_6-C_7-C_6 carbon skeleton, and compound XVII may also be derived via the acyclic precoursor having above carbon skeleton.

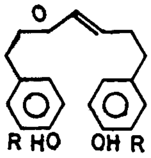
Group A: Acyclic Structure



I. R_1=OH, R_2=H, OH
E-3 (hannokinol)
III. R_1=OH, R_2=H_2, E-9
(+)-centrolobol
VIII. R_1=H, R_2=H_2

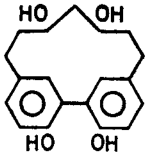


II. R_1=OH,R_2=R_3=OH
E-4 (hannokinin)
platyphyllonol
IV. R_1=R_2=OH, R_3=H
hirsutanonol
VI. R_1=R_2=OH, R_3=xylosyl
oregonin
IX. R_1=R_2=R_3=H, $\Delta^{1,2}$
yashabushi ketol
X. R_1=R_2=R_3=H
dihydroyashabushi ketol

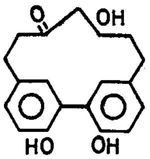


V. R=OH, hirsutenone
VII. R=H

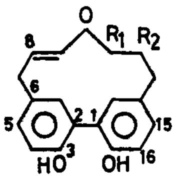
Group B: Cyclic Structure



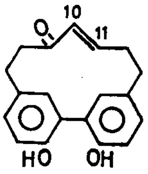
XI. E-5, alnusdiol



XII. E-7, alnusonol

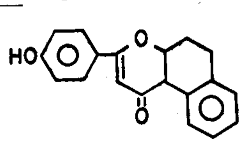


XIII. $R={}_1R_2=H_2$, E-1
XVI. R_1=R_2=H, OH
C^8=H, OH, asadanin

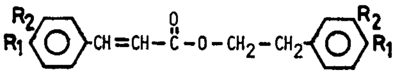


XIV. alnusone
XV. $C^{10,11}$=epoxy

Group C: Others



XVII. E-6



XVIII. R_1=OH, R_2=OMe
E-2 (hannoki ester)
XIX. R_1=R_2=H
β-phenylethyl cinnamate

The occurrence of diarylheptanoids and related compounds in *Betulaceae* is shown in Table 2.

This information indicates that the open chain diarylheptanoids hannokinol I and hannokinin II with monohydroxylated phenyl moiety as the pendant group in the wood of *A. hirsuta* coexist with the corresponding m, m′-bridged compounds

XI and XII, which would clearly be formed from an acyclic material via oxidative coupling catalyzed by peroxidase. However, those of the green bark in the same tree have *o*-dihydroxyphenyl moiety, IV and V[6]. Therefore hannokinin II and hirsutanonol IV appear to have an alternative biogentic process in xylem and phloem to each other. On the other hand, a compound with *o*-dihydroxyphenyl group VI (oregonin) has been isolated from the wood of red alder *A. rubra* as xyloside. KARCHESY *et al.* has pointed out that oregonin is involved in the formation of red-orange chromophores, perhaps by peroxidase catalysis[7].

Both types of the open chian and meta-bridged structure could be found in xylem of *A. hirsuta* and these compounds also have monohydroxylated phenyl group as the partial structure. This is similary mentioned for the extractives from the wood of hannoki *A. japonica*[3,4]. The constituents in the organs other than wood such as buds and leaves, on the contrary, merely are comprised of those with an acyclic carbon skeleton. The substaces from the green bark of *A. hirsuta* have *o*-dihydroxyphenyl group. It is interesting that those of the organ other than wood in *A. firma, A. fruticosa* and *A. mandshurica* are not subjected to hydroxylation on phenyl group. The buds of *A. firma* contain yashabushi ketol IX and dihydroyashabushi ketol X[1]. On the other hand, the leaves of *A. fruitcosa* and *A, mandshurica* have compound VIII[1]. These substances have all open chain structure. Such phenomenone has also been observed in compounds other than diarylheptanoid. β-Phenylethyl cinnamate XIX from the buds of *A. firma* has merely phenyl pendant group, wherease the corresponding hannoki ester XVIII is subjected to hydroxylation and methoxylation on phenyl group[1].

As shown in Table 2, diarylheptanoids are widely distributed over the genera in the same family. Therefore, the occurrence of these compounds appears to be a characteristic feature of *Betulaceae.*

Betulaceae has generally been divided into two tribus *Betuleae* and *Coryleae.* The former includes two genera *Alnus* and *Betula,* on the other hand the latter comprises of four genera *Carpinus, Corylus, Ostrya* and *Ostryopsis*[8]. The green bark of shirakanba *Betula platyphylla* which is grouped into *Betuleae* likewise *Alnus* contain a phenolic platyphyllonol[9] and this compound has an acyclic structure in agreement with hannokinin II. The main constituents of the wood extractives of asada *Ostrya japonica* (*Coryleae*) are asadanin XVI and its homologous having the m, m'-bridged structure and the open chain compounds are not found to date[10]. Recently some phenolics have been isolated from the wood of akashide *Carpinus laxiflora* (*Coryleae*) and one of them has the cyclic structure. The physicochemical natures of this compound is in excellent agreement with those of compound XIII (E-1)[11]. Furthermore, this substance could be found in the extractives from the woods of kumashide *C. japonica* and inushide *C. tshonoskii* on TLC. This peculiarity of structure and substituent groups for the extractives could be detected among species and beyond genera in *Betulaceae.*

4. Conclusion

It has become apparent that diarylheptanoids are the characteristic substances in *Alnus* species and are widespread in the genera in *Betulaeceae.* Furthermore, both of the open chain and m, m′-bridged structures with monohydroxylated phenyl group occur in the wood of *A. hirsuta* and *A. japonica.* On the other hand, those in the green bark of *A. hirsuta* could be found to be an acyclic compound having *o*-dihydroxylated phenyl group as the partial structure. The behaviours of hydroxylation between each organ seem to interpret that an alternative biogenetic process on the formation of those compounds exist in tree.

These compounds could also be found in the genera *Betula, Carpinus* and *Ostrya* in the same family. The green bark of *Betula platyphylla* (*Betuleae*) contains merely the acyclic substance, but the wood of *Carpinus laxiflora* and *Ostrya japonoca* (*Coryleae*) has only the cyclic componds.

Consequently, it is very interesting with regard to chemotaxonomy that the occurrence of diarylheptanoids in *Betulaceae* plays a role of taxonomic marker, although the extractives of the tribus *Coryleae,* except the genus *Ostrya,* has not be satisfactorily investigated.

References

1) SASAYA, T. and IZUMIYAMA, K.: "Phenolic compounds from the wood of Keyamahannoki *Alnus hirsuta* TURCZ. (*Betulaceae*)"., *Res. Bull. College Forest Experi., Hokkaido Univ.,* **31**, 23 (1974).
2) CRAVEIRO, A. A., DA COSTA PRADO, A., GOTTLIEB, O. R. and WELERSON DE ALBUQUERQUE: "Diarylheptanoids of *Centrolobium* species", *Phytochem.* **9**, 1869 (1970).
3) NOMURA, M., TOKOROYAMA, T. and KUBOTA, T.: "Further phenolic Components from *Alnus japonica* STEUD"., *J.C.S. Chem. Comm.,* 316 (1975).
4) NOMURA, M., TOKOROYAMA, T. and KUBOTA, T.: "Three new cycliged C_9-C_1-C_9 compounds from *Alnus japonica* STEUD"., *ibid.,* 65 (1974).
5) EDWARDS, J. M., SCHMITT, R. C. and WEISS, U.: "Biosynthesis of 9-phenylperinaphthenone by *Lachnanthes tinctoria*", *Phytochem.* **11**, 1717 (1972).
6) TERAZAWA, M., KOGA, T., OKUYAMA, H. and MIYAKE, M.: "Isolation of hirsutanonol and hirstenone, two new diarylheptanoids from the green bark Keyamahannoki, *Alnus hirsuta* TURCZ.." *Mokuzai Gakkaishi,* **19**, 45 (1973).
7) KARCHESY, J. J., LAVER, M. M., BAROFSKY, D. F. and BAROFSKY, E.: "Structure of Oregonin, a Natural Diarylheptanoid Xyloside", *J.C.S. Chem. Comm.,* 649 (1974).
8) HEGNAUER, R.: "Chemotaxonomie der Pflanzen", Birkhäseur Verlag, Band 3, p. 255 (1964).
9) TERAZAWA, M., KOGA, T., OKUYAMA, H. and MIYAKE, M.: "Isolation of platyphyllonol, a new diarylheptanoid from the green bark of Shirakanba, *Betula platyphylla* SUKATCH var. *japonica* HARA", *Mokuzai Gakkaishi* **19**, 47 (1973).
10) YASUE, M.: "Studies on the wood extractives of *Ostrya japonica* —On the chemical structures of asadanin and its related compounds", *Bull.* of the Government Forest Experiment Station, No. 209 (1968).
11) SASAYA, T.: "Extractives of of *Carpinus* species —phenolics of *C. laxiflora*—", Presented at the 34th Annual Meeting of the Japan Wood Research Society at Nagoya, April 1984.

摘　要

ケヤマハンノキ *Alnus hirsuta* TURCZ 材のアルコール抽出物の検索を行い，新たに4種のフェノール成分 III(E-9), XI(E-5), XII(E-7) および XVII(E-6) を単離した。既に報告した3種の化合物 I(E-3), II(E-4) および XIII(E-1) と共にジアリルヘプタノイドの構造を有する。その物理化学的状から化合物IIIはグループAに，XIおよびXIIはグループBに，XVIIはグループCに分類される。

これらの化合物およびその誘導体の呈色反応，元素分析およびスペクトロスコピーの結果より，化合物E-9は 1,7-di-(*p*-hydroxyphenyl)-heptan-3-ol (III)，化合物E-5およびE-7は各々構造式XIおよびXIIと同定した。一方，化合物E-6は構造式XVIIと推定され，基本骨格 tetrahydronaphthoflavone 構造を有し，この化合物の知見は未だ得られていない。

いずれも化合物I, IIおよびXIIIと同様ジアリルヘプタノイドならびに関連物質である。化合物IIIは open chain 構造 (acyclic) を有する。一方，化合物XIおよびXIIは m, m′-bridged 構造 (cyclic) を有し，これに相当する acyclic の化合物IおよびIIと共に得られた事は興味がある。また，化合物XVIIはかなり複雑に還化しているが，*Lachanthes tinctoria* の根から得た 9-phenylperinaphthenone と類似した生合成の結果生じたものと推定される。

ケヤマハンノキ材は monohydroxylated 置換の acyclic および cyclic の両タイプの成分を含有する。これと同様な結果はハンノキ *A. japonica* 材のジアリルヘプタノイドについても見られる。しかし，同一樹種でも部位が異なると，例えばケヤマハンノキの green bark は ortho-dihydroxylated 構造Vが現われる。他の組織では更に置換分の変化が認められる。ヤシャブシ *A. firma* の buds や *A. fruticosa* および *A. mandshurica* の leaves では水酸基置換を有しないフェニル核をもつ成分 (IX, X および VIII) を生ずる。材以外の部位ではcyclic 構造の成分は未だ得られていない。ジアリルヘプタノイド以外の成分についても置換分の異なる結果がケヤマハンノキ材 (XVIII) とヤシャブシの buds (XIX) に観察される。

この種の化合物はハンノキ属だけでなく *Betulaceae* の各属にわたって認められる。ハンノキ属と同じ tribus *Betuleae* に入るカバノキ属の *Betula plathyphylla* の green bark は化合物IIと同様の acyclic monohydroxylated 構造をもつ plathyphyllonol を含有するが，cyclic 構造の成分の知見が得られていない。

一方，tribus *Coryleae* 中のアサダ *Ostrya japonica* 心材は特徴的な m, m′-bridged 構造の asadanin (XVI) およびその同族体を含有するが，open chain 構造の成分の存在の知見を得ていない。同じ *Coryleae* に属するクマシデ属のアカシデ *Carpinus laxiflora* 材より得た成分は化合物 XIII(E-1) と同定された。この成分はクマシデ *C. japonica* およびイヌシデ *C. tshnoskii* 材の抽出物中にも存在する事が TLC 上で確認された。しかし，現在までにアサダと同様，acyclic 構造に相当する成分を得ていない。

これらのジアリルヘプタノイドはカバノキ科の樹種間，同一樹種でも異なる部位間さらに属間にわたって特異的に存在する。更に精査が必要であるけれど，tribus 間においてもこれらの化合物は 1 つの taxonomic marker としての役割を演ずる事ができると推察される。