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Indonesian Medicinal Plants. I. New Furanoditerpenes from *Arcangelisia flava* MERR. (1)

TOSHINOBU KUNII, KENGO KAGEI,* YOSHIYUKI KAWAKAMI,
YASUSHI NAGAI, YUKUO NEZU,
and TADASHI SATO

Tsukuba Research Laboratories, Eisai Co., Ltd.,
1-3, Tokodai 5-chome, Toyosato-machi,
Tsukuba-gun, Ibaraki 300-26, Japan

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Four new furanoditerpenes, 6-hydroxyarcangelisin (**1a**), 2-dehydroarcangelisinol (**2**), tinophyllol (**3a**) and 6-hydroxyfibleucin (**4b**), which were isolated from the Indonesian traditional medicinal plant, *Arcangelisia flava* MERR. (Menispermaceae), have been shown to have the structures illustrated in Chart 1. Fibraurin (**5a**), 6-hydroxyfibraurin (**5d**) and fibleucin (**4a**), which were isolated from the same plant extract, were also identified.

Assignments of the ^{13}C-nuclear magnetic resonance signals of the isolated furanoditerpenes and their derivatives were carried out.

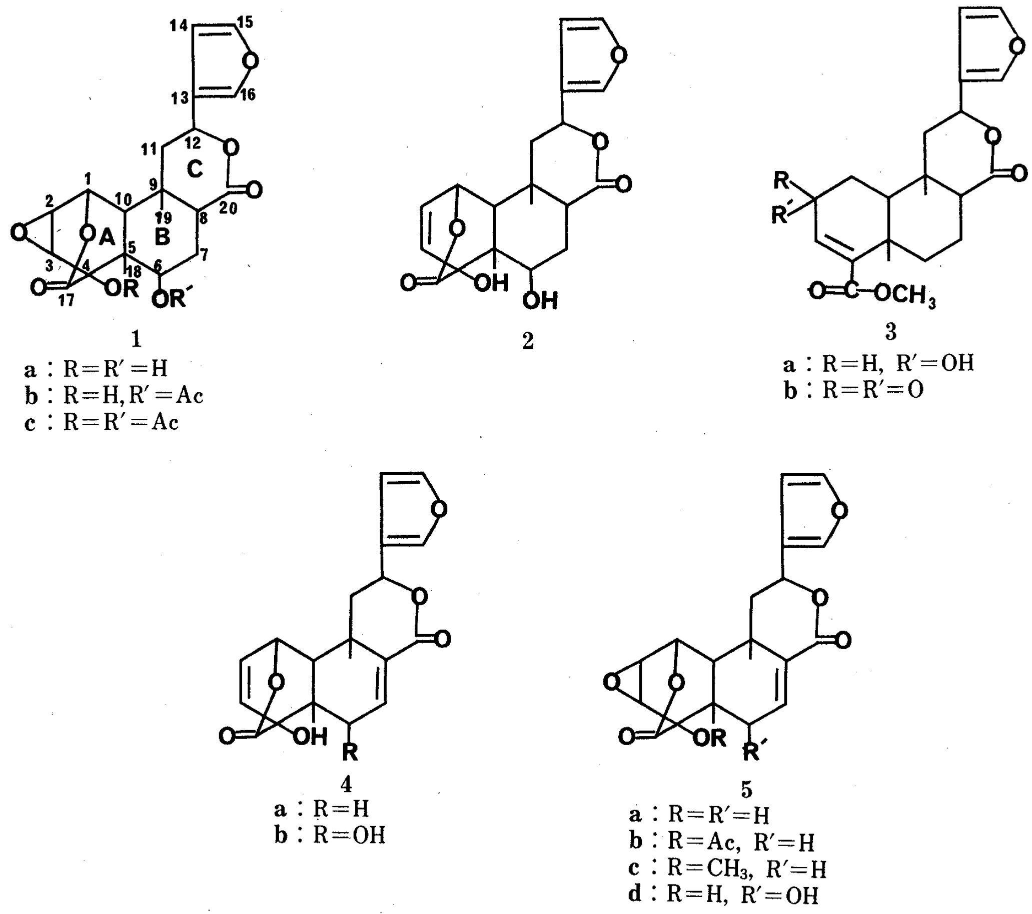
Keywords——*Arcangelisia flava*; Menispermaceae; furanoditerpene; Indonesian medicinal plant

The stem of *Arcangelisia flava* MERR. (Menispermaceae) is an important component of folk medicine (Indonesian name: Jamu) in Indonesia. The ethyl acetate-soluble part of the methanol extract of *A. flava*, was subjected to column chromatography to give 13 furanoditerpenes. This paper describes the structural elucidation of the four new furanoditerpenes, 6-hydroxyarcangelisin (**1a**), 2-dehydroarcangelisinol (**2**), tinophyllol (**3a**), and 6-hydroxyfibleucin (**4a**), and the identification of fibleucin (**4a**),[2] fibraurin (**5a**)[1] and 6-hydroxyfibraurin (**5d**)[1] (Chart 1).

Various furanoditerpenes, including fibraurin **5a**,[1] 6-hydroxyfibraurin **5d**,[1] fibleucin **4a**,[2] chasmantin,[3,5c,6] palmalin,[4,5b,c] columbin,[4,5] jateorin,[5c] isojateorin,[4,5c] and tinophyllon[7] from Menispermaceae plants, salivarin[8] from a Labiatae plant, and diasin[9] from a Euphorbiaceae plant, have already reported. However, carbon-13 nuclear magnetic resonance (^{13}C-NMR) data for these furanoditerpenes have not been reported. In this study, assignments of the ^{13}C-NMR signals of furanoditerpenes isolated from *A. flava* and their derivatives were carried out.

6-Hydroxyarcangelisin (1a)

$C_{20}H_{22}O_8$, $[\alpha]_D^{20}+55.27°$ (pyridine, $c=0.54$), mp 274 °C (dec.). The infrared (IR) spectrum of (**1a**) showed two carbonyl absorption bands (1780 and 1705 cm^{-1}, δ-lactones) and a β-substituted furan ring (1508, 1022, 875 and 812 cm^{-1}). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum (Fig. 1) of **1a** showed an epoxy group and hydroxy groups involved in intramolecular hydrogen bond formation (based on the IR spectrum). Detailed 400 MHz ^{1}H-NMR decoupling experiments disclosed that **1a** has the same A- and C-ring partial structure as fibraurin **5a**[1]: 1) two epoxide protones at δ 3.88 and δ 3.67 were coupled ($J=4.4$ Hz) and a low field signal (δ 3.88) was coupled to a proton at 5.00 (C_1-H) ($J=2.5$ Hz); 2) C_{12}-H (a double-doublet at δ 5.46, $J=12.1$, 4.0 Hz; X of ABX) was coupled to the



1
a : R=R'=H
b : R=H, R'=Ac
c : R=R'=Ac

2

3
a : R=H, R'=OH
b : R=R'=O

4
a : R=H
b : R=OH

5
a : R=R'=H
b : R=Ac, R'=H
c : R=CH3, R'=H
d : R=H, R'=OH

Chart 1

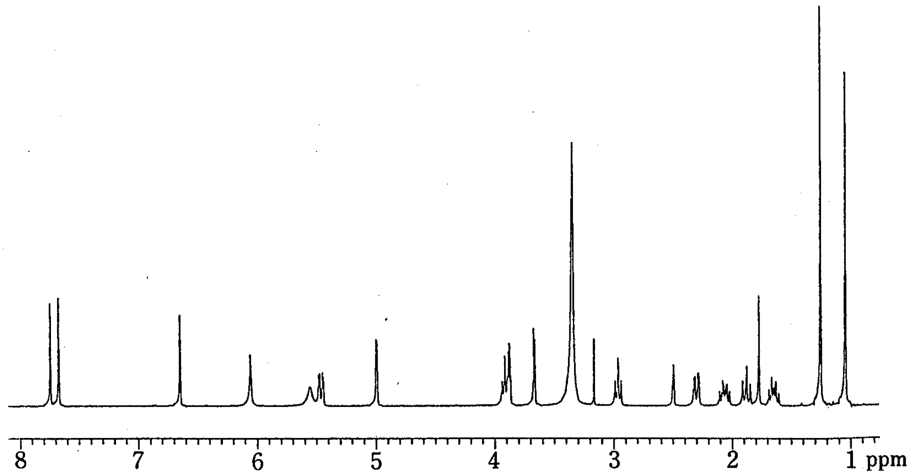
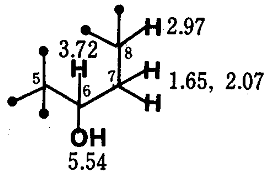


Fig. 1. ^{1}H-NMR Spectrum of **1a** (in DMSO-d_6)

methylene group of C_{11} at δ2.31 and δ1.88 (two double-doublets; AB of ABX), and this 12.1 Hz coupling constant indicated that C_{12}-H is axially oriented. These ^{1}H-NMR data for **1a** showed that a furan ring was located at the C_{12} position as in fibraurin **5a**[1] and 6-hydroxyfibraurin **5d**.[1]

In addition, the ^{1}H-NMR data for **1a** showed two proton signals at δ6.06 (singlet) and δ5.54 (d, $J=3.3$ Hz) which disappeared upon addition of D_2O. The signal at δ6.06 was



C_6-OH, C_6-H, $J=3.3$ Hz
C_6-H, C_7-CH_2, $J=8.8$ Hz
C_7-CH_2, C_8-H, $J=9.9$ Hz

Fig. 2. Chemical Shift and Coupling Constants in the B-Ring of **1a**

assigned to a tertiary hydroxy group (attached to C_4); this was supported by the observation that this signal (δ 6.06) was absent in the diacetate (**1c**).

The doublet at δ 5.54 was attributable to a secondary hydroxy group, because this proton (δ 5.54) was coupled to the C_6-H methine signal (δ 3.92, td, $J=3.3$, 8.8 Hz) and was still seen in the monoacetate (**1b**). In addition, the C_6-H signal changed to a triplet ($J=8.8$ Hz) on adding D_2O and in irradiation experiments. This signal at δ 3.92 was thus coupled to adjacent C_7 methylene protons (δ 1.65 and δ 2.07), which were coupled to C_8-H (δ 2.97, t) with $J=9.9$ Hz. These data suggest the partial structure depicted in Fig. 2. In order to assign the carbons of **1a**, ^{13}C-NMR examination was carried out (Table II). ^{13}C-NMR assignment was based on the results of proton noise complete decoupling (COM), off-resonance decoupling (OFR) and selective proton decoupling (SEL). The ^{13}C-NMR data supported the above result: 1) the presence of two methylene carbon signals (δ 27.3 and δ 43.2) was observed, of which the lower field signal (δ 43.2, t) was assigned to C_{11} and the higher field signal (δ 27.3, t) to C_7, 2) the signal at δ 69.3 (d) was assigned to a carbon (C_6) having a secondary hydroxy group.

Thus, the structure of **1a** was concluded to be as shown in Chart 1.

2-Dehydroarcangelisinol (2)

$C_{20}H_{22}O_7$, $[\alpha]_D^{20}+98.8°$ (pyridine, $c=0.5$). The IR spectrum of (**2**) showed two carbonyl absorption bands (1772 and 1715 cm^{-1}, δ-lactones), together with hydroxy bands (3370 and 3285 cm^{-1}) and absorptions due to a β-substituted furan ring (1510, 875 and 808 cm^{-1}). The furan ring was located at C_{12}, since the chemical shifts and coupling constants in the ^1H-NMR were quite similar among **1a**, **4a**, **4b**, **5a** and **5d** (Table I). The ^1H-NMR spectrum of **2** showed signals (δ 6.53, dd, $J=8.0$, 5.0 Hz; δ 6.14, dd, $J=8.0$, 1.8 Hz) due to α,β-disubstituted double bond protons. The ^{13}C-NMR data (δ 131.2, d; δ 135.0, d) supported this interpretation. It was confirmed that the lower field signal (δ 6.53) was due to C_2-H, and that the other (δ 6.14) was C_3-H by irradiation of C_1-H (δ 5.26, dd, $J=5.0$, 1.8 Hz). Further, two signals (δ 5.84, s and δ 5.59, d, $J=4.0$ Hz) which disappeared on the addition of D_2O showed the presence of hydroxy groups in this molecule. The signal (δ 4.00, 1H, ddd, $J=9.0$, 8.0, 0.4 Hz) of C_6-H changed to double-doublet form ($J=9.0$, 8.0 Hz, coupled to C_7-methylene) on irradiation of the secondary hydroxy proton (δ 5.59). Accordingly, the structure for **2** was concluded to be as shown in Chart 1.

Tinophyllol (3a)

$C_{21}H_{26}O_6$, $[\alpha]_D^{20}-19.3°$ (pyridine, $c=0.5$). The IR spectrum of (**3a**) showed the presence of two carbonyl absorption bands (1730 and 1718 cm^{-1}), and a β-substituted furan ring (1495, 878 and 815 cm^{-1}), which was further supported by the ^1H-NMR data (Table I). The ^1H-NMR spectrum of **3a** showed the presence of tertiary methyl groups (δ 0.84 and δ 1.32), a methoxy group (δ 3.68, 3H) and an olefinic proton (1H, δ 4.34, ddd, $J=4.0$, 8.0, 0.8 Hz). From these data and the molecular formula, two carbonyl groups of **3a** were assigned to a lactone and methyl ester. The C-ring of **3a** had the same structure as that of fibraurin **5a**, 6-hydroxyfibraurin **5d** and 6-hydroxyarcangelisin **1a** from the chemical shifts and coupling

Table I. ¹H-NMR Data for Furanoditerpenes and Their Derivatives from *Arcangelisia flava*

Carbon	**1a**		**1b**		**1c**		**2**		**3a**		**3b**	
	CS[a)]	*J*	CS[a)]	*J*	CS[a)]	*J*	CS[a)]	*J*	CS[a)]	*J*	CS[a)]	*J*
1	5.00 d	2.5	5.01 d	2.5	5.13 d	2.5	5.26 dd	5.0, 1.8	1.93 ddd 2.14 dd	14.0, 6.0, 8.0 8.0, 14.0	2.45 d 2.99 dd	19.0 19.0, 6.0
2	3.88 dd	2.5, 4.4	3.88 dd	2.5, 4.4	3.96 dd	2.5, 4.4	6.53 dd	5.0, 8.0	4.96 br s 4.34 ddd	 4.0, 8.0, 8.0		
3	3.67 d	4.4	3.61 d	4.4	3.95 d	4.4	6.14 dd	8.0, 1.8	6.25 d	4.0	6.12 s	
4-OH	6.06 s		5.97 s				5.84 s					
4-OMe									3.68 s		3.78 s	
4-OAc					2.17 s							
6	3.92 td	3.3, 8.8	4.89 t	8.8	4.98 t	8.8	4.00 ddd	4.0, 8.0, 9.0	2.43 dd 1.18	3.0, 11.0	2.16 1.29	
6-OH	5.54 d	3.3					5.59 d	4.0				
6-OAc			1.97 s		2.07 s							
7	1.65 m 2.07 m		1.66 m 2.08 m		1.72 m 2.22 m		1.66 m 2.10 m		1.18 1.61 m		1.37 1.70	
8	2.97 t	9.9	3.00 t	10.0	3.01 t	10.0	2.90 t	9.9	2.79 dd	3.0, 10.0	2.88 dd	11.0 3.0
10	1.78 s		1.84 s		1.94 s		1.59 s		1.80 d	6.0	2.22 d	6.0
11	1.88 dd 2.31 dd	13.5, 12.1 13.5, 4.0	1.90 dd 2.36 dd	13.0, 12.0 13.0, 4.0	1.96 dd 2.39 dd	13.0, 12.0 13.0, 4.0	1.88 dd 2.34 dd	12.0, 13.5 13.5, 4.0	2.06 dd 1.87 dd	14.0, 6.0 14.0, 12.0	2.02 dd 1.86 dd	14.0, 6.0 14.0, 12.0
12	5.46 dd	4.0, 12.1	5.48 dd	4.0, 12.0	5.49 dd	4.0, 12.0	5.47 dd	12.0, 4.0	5.49 dd	12.0, 6.0	5.50 dd	12.0, 6.0
14	6.65 d	1.8	6.64 d	1.8	6.62 d	1.8	6.63 d	1.8	6.55 d	1.8	6.56 d	1.8
15	7.68 dd	1.6, 1.8	7.68 dd	1.6, 1.8	7.64 dd	1.6, 1.8	7.63 dd	1.6, 1.8	7.68 dd	1.6. 1.8	7.65 dd	1.6, 1.8
16	7.75 d	1.6	7.75 d	1.6	7.72 d	1.6	7.72 d	1.6	7.73 d	1.6	7.74 d	1.6
18	1.26 s		1.38 s		1.44 s		1.06 s		1.32 s		1.42 s	
19	1.05 s		1.07 s		1.07 s		1.03 s		0.84 s		0.70 s	

TABLE I. (continued).

Carbon	4a		4b		5a		5b		5c		5d	
	CS[a)]	J	CS[a)]	J	CS[a)]	J	CS[a)]	J	CS[a)]	J	CS[a)]	J
1	5.38 dd	5.0, 1.8	5.35 dd	5.0, 1.8	5.09 d	2.9	5.21 d	2.9	5.14 d	2.9	5.10 d	2.9
2	6.55 dd	5.0, 8.0	6.57 dd	5.0, 8.0	3.87 dd	4.2, 2.9	3.98 m		3.93 dd	4.2, 2.9	3.91 dd	4.2, 2.9
3	6.25 dd	8.0, 1.8	6.21 dd	8.0, 1.8	3.67 d	4.2	3.98 m		4.06 d	4.2	3.74 d	4.2
4-OH	6.26 s		6.00 s		6.50 s						6.34 s	
4-OMe									3.61 s			
4-OAc							2.18 s					
6	2.42 dd 1.87 dd	17.0, 8.0 17.0, 2.7	4.47 dd	3.0, 2.0	2.34 dd 1.71 dd	17.0, 8.0 17.0, 2.8	2.35 dd 1.81 dd	17.0, 8.0 17.0, 2.8	2.35 dd 1.77 dd	17.0, 8.0 17.0, 2.8	4.33 d	2.8
6-OH			5.65 d	3.0							5.51 br s	
6-OAc												
7	7.27 dd	8.0, 2.7	6.89 d	2.0	7.25 dd	8.0, 2.8	7.23 dd	8.0, 2.8	7.24 dd	8.0, 2.8	6.86 d	2.8
8												
10	1.67 s		1.79 s		1.79 s		1.87 s		1.82 s		1.90 s	
11	2.00 dd 2.35 dd	14.0, 12.0 14.0, 2.0	2.00 dd 2.32 dd	13.0, 12.0 13.0, 2.5	1.95 dd 2.32 dd	14.0, 12.0 14.0, 2.5	2.00 dd 2.33 dd	14.0, 12.0 14.0, 2.5	1.99 dd 2.33 dd	14.0, 12.0 14.0, 2.5	2.04 dd 2.29 dd	14.0, 12.0 14.0, 2.0
12	5.67 dd	12.0, 2.0	5.68 dd	12.0, 2.5	5.67 dd	12.0, 2.5	5.68 dd	12.0, 2.5	5.68 dd	12.0, 2.5	5.68 dd	12.0, 2.0
14	6.65 d	1.8	6.62 d	1.8	6.64 d	1.8	6.63 d	1.8	6.66 d	1.8	6.64 d	1.8
15	7.68 dd	1.6, 1.8	7.62 dd	1.6, 1.8	7.67 dd	1.6, 1.8	7.68 dd	1.6, 1.8	7.68 dd	1.6, 1.8	7.69 dd	1.6, 1.8
16	7.78 d	1.6	7.74 d	1.6	7.76 d	1.6	7.76 d	1.6	7.77 d	1.6	7.76 d	1.6
18	0.93 s		0.99 s		1.08 s		1.15 s		1.10 s		1.16 s	
19	1.18 s		1.18 s		1.17 s		1.15 s		1.18 s		1.18 s	

a) Chemical shift (ppm from internal TMS in DMSO-d_6).

Table II. ^{13}C-NMR Data for Furanoditerpenes and Their Derivatives from *Arcangelisia flava*

	1a	**1b**	**1c**	**2**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**5c**	**5d**
C-1	69.2 d	69.1 d	69.6 d	72.9 d	28.6 t	35.4 t	73.8$^{c)}$ d	73.5$^{c)}$ d	69.7 d	69.6 d	69.5 d	69.9 d
C-2	49.1 d	49.3 d	50.0$^{c)}$ d	131.2 d	62.5 d	197.6 s	130.6 d	131.0 d	49.5 d	50.3 d	48.6 d	49.4 d
C-3	50.5 d	51.5 d	50.5$^{c)}$ d	135.0 d	139.3 d	130.4 d	137.0 d	135.9 d	51.6 d	50.4 d	48.6 d	51.1 d
C-4	82.7 s	81.2 s	85.5 s	82.8 s	138.7 s	157.1 s	80.3 s	81.9 s	80.0 s	84.1 s	85.6 s	82.0 s
C-5	34.8 s	34.9 s	34.9 s	35.5 s	36.0 s	37.2 s	35.6 s	35.6 s	35.2 s	35.2 s	35.1 s	35.2 s
C-6	69.3 d	70.3 d	69.8 d	70.0 d	43.9$^{b)}$ t	37.2 t	31.1 t	71.1$^{c)}$ d	31.2 t	31.0 t	31.0 t	70.2 d
C-7	27.3 t	25.7 t	25.6 t	28.2 t	19.7 t	19.6 t	142.1 d	146.6 d	142.1 d	141.2 d	141.7 d	145.8 d
C-8	43.1 d	42.8 d	42.5 d	44.3 d	47.0 d	45.8 d	134.3 s	132.1 s	133.3 s	133.3 s	133.2 s	131.1 s
C-9	43.4 s	43.8 s	44.6 s	40.2 s	36.9 s	42.8 s	42.4 s	46.5 s	44.8 s	44.7 s	44.9 s	48.7 s
C-10	55.5 d	56.3 d	56.3 d	57.5 d	54.2 d	52.1 d	55.9 d	57.3 t	54.0 d	53.8 d	54.2 d	55.1 d
C-11	43.2 t	42.8 t	42.6 t	43.7 t	34.8$^{b)}$ t	34.6 t	42.1 t	41.8 t	42.0 t	41.6 t	41.8 t	42.0 t
C-12	71.3 d	71.5 d	71.6 d	71.9 d	69.4 d	69.3 d	69.7$^{c)}$ d	69.9$^{c)}$ d	70.6 d	71.3 d	70.5 d	71.0 d
C-13	125.2 s	125.2 s	125.0 s	125.4 s	124.6 s	124.3 s	125.0 s	124.8 s	125.0 s	124.9 s	108.9 d	124.8 s
C-14	109.1 d	109.1 d	109.0 d	109.5 d	109.2 d	109.3 d	109.1 d	109.1 d	109.1 d	108.9 d	124.9 s	109.0 d
C-15	140.4 d	140.5 d	140.3 d	140.7 d	140.1 d	140.4 d	140.4 d	140.5 d	140.4 d	140.4 d	140.3 d	140.4 d
C-16	143.8 d	143.9 d	143.7 d	144.1 d	143.8 d	143.9 d	143.8 d	143.8 d	143.9 d	143.8 d	143.8 d	143.9 d
C-17	171.4 s	171.5$^{a)}$ s	168.8$^{a)}$ s	172.4$^{a)}$ s	168.0$^{a)}$ s	173.8$^{a)}$ s	163.2$^{a)}$ s	162.4$^{a)}$ s	163.2$^{a)}$ s	168.5$^{a)}$ s	169.1$^{a)}$ s	168.4$^{a)}$ s
C-18	17.2 q	19.0$^{b)}$ q	18.9$^{b)}$ q	18.1$^{b)}$ q	33.2 q	31.6 q	26.4$^{b)}$ q	20.8$^{b)}$ q	25.0$^{b)}$ q	25.1$^{b)}$ q	25.1$^{b)}$ q	21.3$^{b)}$ q
C-19	18.4 q	18.3$^{b)}$ q	18.2$^{b)}$ q	18.6$^{b)}$ q	22.7 q	22.4 q	20.4$^{b)}$ q	19.4$^{b)}$ q	20.7$^{b)}$ q	20.4$^{b)}$ q	20.6$^{b)}$ q	18.4$^{b)}$ q
C-20	171.7 s	170.7$^{a)}$ s	168.4$^{a)}$ s	174.9$^{a)}$ s	174.2$^{a)}$ s	167.1$^{a)}$ s	174.6$^{a)}$ s	174.2$^{a)}$ s	171.5$^{a)}$ s	162.9$^{a)}$ s	162.9$^{a)}$ s	171.1$^{a)}$ s
4-O$\underline{C}$H$_3$					51.5 q	52.4 q					54.0 q	
4-$\underset{\overset{\|}{O}}{\underline{C}}$-CH$_3$		169.3$^{a)}$ s	165.7$^{a)}$ s							166.5 s		
4-$\underset{\overset{\|}{O}}{C}$-$\underline{C}H_3$		21.3 q	20.8 q							20.6$^{b)}$ q		
6-$\underset{\overset{\|}{O}}{\underline{C}}$-CH$_3$			171.3$^{a)}$ s									
6-$\underset{\overset{\|}{O}}{C}$-$\underline{C}H_3$			20.8 q									

δ ppm from internal TMS in DMSO-d_6.

a—*c*) These assignments may be reversed in each column.

constants (δ 5.49, dd, $J=12.0$, 6.0 Hz) of C_{12}-H. On the other hand, the ^{13}C-NMR spectrum of **3a** showed the presence of four methylene groups (δ 19.7, 28.6, 34.8 and 43.9) and a trisubstituted double bond (δ 139.3, d and 138.7, s) at $C_{3(4)}$. Based on the above results, possible locations of the double bond in **3a** were presumed to be $C_{1(10)}$, $C_{3(4)}$, or $C_{7(8)}$. Fortunately, a direct correlation between tinophyllol **3a** and tinophyllon **3b**$^{7)}$ was readily accomplished by the following reaction; chromic oxidation of **3a** afforded an enone that was identical with an authentic sample **3b**$^{7)}$ on the basis of mp, thin layer chromatography (TLC), ultraviolet (UV) and ^{1}H- and ^{13}C-NMR spectral comparisons. Thus, the hydroxy group and the double bond of **3a** were established to be located at C_2 and $C_{3(4)}$, respectively. Therefore, **3a** was the C_2 carbonyl-reduced derivative of **3b**.

6-Hydroxyfibleucin (4b)

$C_{20}H_{20}O_7$, $[\alpha]_D^{20}+59.1°$ (pyridine, $c=0.49$). The ^{1}H-NMR spectrum of (**4b**) showed disubstituted double bond signals (δ 6.57, 1H, dd, $J=5.0$, 8.0 Hz; δ 6.21, 1H, dd, $J=8.0$, 1.8 Hz; C_2-H and C_3-H), which were confirmed by decoupling of C_1-H (δ 5.35, 1H, dd, $J=5.0$, 1.8 Hz). Compound **4b** possessed one more oxygen atom than fibleucin **4a**, and **4b** and **4a** (Tables I and II) showed very similar A- and B-ring signals. This oxygen atom was concluded to be in a hydroxy group from the ^{1}H-NMR data (δ 5.65, d, $J=3.0$ Hz, disappeared on adding D_2O). The location of this hydroxy group was determined by the observation that hydrogen of this hydroxy group was coupled with C_6-H (δ 4.47, dd, $J=2.0$, 3.0 Hz), which was also coupled with a vinyl proton (δ 6.87, d, $J=2.0$ Hz; C_7-H) as confirmed by a decoupling experiment. In the ^{13}C-NMR, the signal (δ 71.1, d) due to C_6 was in good accord with that of 6-hydroxyfibraurin **5d**.$^{1)}$ Thus, **4b** was concluded to be 6-hydroxyfibleucin.

Finally, three compounds **5a**, **5d** and **4a** were isolated from the ethyl acetate-soluble fraction of *A. flava*. Compounds **5a**, **5b**, **5c** and **5d** were identified as fibraurin,$^{1)}$ fibraurin acetate,$^{1)}$ methylfibraurin$^{1)}$ and 6-hydroxyfibraurin,$^{1)}$ respectively. All these compounds were identified on the basis of mp, $[\alpha]_D$, and UV, IR and ^{1}H-NMR spectra. In addition, **4a** was confirmed to be fibleucin$^{2)}$ by direct comparison with an authentic sample (mp, and IR, UV and ^{1}H-NMR spectra).

Further work is in progress on the structural elucidation of other new furanoditerpenes from *A. flava*, and the stereochemistry of the isolated furanoditerpenes, and will be reported elsewhere.

Experimental

The following instruments were used for measuring the physical data: mp, Yanagimoto micro melting point hot stage apparatus (values are uncorrected); UV, Shimadzu UV-210; IR, Hitachi EPI-G3; NMR, JEOL JNM-GX-400; Mass spectrometry (MS), JMS-DX-300; RD, JASCO DIP-4 polarimeter.

^{1}H-NMR and ^{13}C-NMR spectra (obtained in DMSO-d_6) data were assigned with the aid of decoupling at 400 MHz. The following abbreviations are used in this paper; s = singlet; d = doublet; dd = double-doublet; ddd = double-double-doublet; t = triplet, q = quartet; m = multiplet. Chemical shifts are expressed in ppm from tetramethyl silane (TMS). Parent peaks in the MS are indicated by M^+.

Isolation of Furanoditerpenes from the Stem of *A. flava*——The pulverized stems (17 kg) of *Arcangelisia flava* MERR. were concentrated under reduced pressure. A small amount of MeOH was added to the residue, and insoluble material was filtered off. The MeOH solution was concentrated, and the residue was partitioned with ethyl acetate–water. The ethyl acetate layer was concentrated to dryness and the residue (150 g) was absorbed on silica-gel. This silica-gel was placed on top of a column of silica-gel and eluted with $CHCl_3$–MeOH mixture by gradually changing the solvent composition from 97 : 3 to 8 : 1. Yields of furanoditerpenes were followed: 6-hydroxyarcangelisin **1a**, 493 mg; 2-dehydroarcangelisinol **2**, 23 mg; tinophyllol **3a**, 144 mg; fibleucin **4a**, 4.2 g; 6-hydroxyfibleucin **4b**, 310 mg; fibraurin **5a**, 4.5 g; 6-hydroxyfibraurin **5d**, 643 mg.

6-Hydroxyarcangelisin (1a)——mp 274 °C (dec.), colorless prisms from MeOH, $[\alpha]_D^{20}+55.27°$ (pyridine, $c=0.54$). *Anal.* Calcd for $C_{20}H_{22}O_8$: C, 61.53; H, 5.68. Found: C, 61.40; H, 5.71. UV λ_{max}^{EtOH} nm; 213. field desorption mass spectra (FD-MS) (m/z): 390 (M^+), electron-impact mass spectra (EI-MS) (m/z): 391 ($M^+ + 1$). IR ν_{max}^{Nujol} cm^{-1}: 3330, 1780, 1705, 1602, 1508, 875, 812. ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

6-Hydroxyarcangelisin Monoacetate (1b)——**1a** (55 mg) was acetylated overnight in 5 ml of pyridine and 5 ml of acetic anhydride at room temperature to give 44 mg of colorless scales, mp 247—250 °C (MeOH). *Anal.* Calcd for $C_{22}H_{24}O_9 \cdot H_2O$: C, 58.66,; H, 5.82. Found: C, 58.41; H, 5.74. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1765, 1740, 1710, 1690, 1508, 875, 810. EI-MS (m/z): 432 (M$^+$), 372 (M$^+$ -60). ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

6-Hydroxyarcangelisin Diacetate (1c)——**1a** (50 mg) was acetylated overnight in 5 ml of pyridine and 5 ml of acetic anhydride at room temperature, then heated in a water bath for 3 h, and poured into ice-water. After extraction with ethyl acetate and recrystallization of the product from MeOH, colorless needles were obtained, mp 230 °C. *Anal.* Calcd for: $C_{24}H_{26}O_{10}$: C, 60.75; H, 5.52. Found: C; 60.61; H, 5.54. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1775, 1754, 1727, 1503, 875, 805. EI-MS (m/z): 475 (M$^+$). ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

2-Dehydroarcangelisinol (2)——mp 208—212 °C (dec.), colorless prisms from MeOH, $[\alpha]_D^{20}$ +98.8° (pyridine, c= 0.25). *Anal.* Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.18; H, 5.98. UV $\lambda_{\max}^{\text{EtOH}}$ nm: 214. FD-MS (m/z): 375 (M$^+$ + 1), EI-MS (m/z): 375 (M$^+$ + 1), 374 (M$^+$). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3370, 3285, 1772, 1708, 1510, 875, 808. ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

Tinophyllol (3)——mp 229—231 °C (dec.), colorless prisms from MeOH, $[\alpha]_D^{20}$ −19.3° (pyridine, c=0.5). *Anal.* Calcd for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.37; H, 7.15. UV $\lambda_{\max}^{\text{EtOH}}$ nm: 216. EI-MS (m/z): 374 (M$^+$). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3470, 3130, 1730, 1718, 1495, 878, 815. ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

Tinophyllon (3b)$^{7)}$——**3a** (50 mg) was dissolved in acetone. Jone's reagent was added, and the mixture was left to stand for 20 minutes at room temperature. Water was added, and the whole was extracted with ethyl acetate. Tinophyllon (**3b**)$^{7)}$ (38 mg) was obtained as colorless needles, mp, 176—179 °C (MeOH). UV $\lambda_{\max}^{\text{EtOH}}$ nm: 212, 240. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1743, 1724, 1672, 1502, 876, 815. ^{1}H-NMR as given in Table I. ^{13}C-NMR as in Table II.

Fibleucin (4a)$^{2)}$——mp 183—185 °C (dec.), colorless prisms from MeOH–CHCl$_3$, $[\alpha]_D^{20}$ −3.1° (pyridine, c=0.5). *Anal.* Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.56. Found: C, 67.48; H, 5.76. UV $\lambda_{\max}^{\text{EtOH}}$ nm: 217, 220. FD-MS (m/z): 356 (M$^+$), EI-MS (m/z): 357 (M$^+$ + 1). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3470, 1765, 1635, 1603, 1502, 875. ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

6-Hydroxyfibleucin (4b)——mp 195—204 °C (dec.), colorless plates from MeOH, $[\alpha]_D^{20}$ −59.1° (pyridine, c= 0.49). *Anal.* Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.53; H, 5.36. UV $\lambda_{\max}^{\text{EtOH}}$ nm: 211, 231. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3300, 1770, 1703, 1637, 1601, 1508, 873, 812. EI-MS (m/z): 373 (M$^+$ + 1), FD-MS (m/z): 373 (M$^+$ + 1), 372 (M$^+$). ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

Fibraurin (5a)$^{1)}$——mp 285 °C (dec.), colorless prisms from dioxane–MeOH, $[\alpha]_D^{20}$ −29.3° (pyridine, c=1.0), *Anal.* Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.38; H, 5.23. UV $\lambda_{\max}^{\text{EtOH}}$ nm: 217, 230. EI-MS (m/z): 372 (M$^+$). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3450, 3125, 1768, 1692, 1632, 1502, 875, 815. ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

Fibraurin Acetate (5b)——**5a** (300 mg) was acetylated overnight at room temperature in 10 ml of pyridine and 10 ml of acetic anhydride to give 160 mg of colorless needles, mp 315 °C (MeOH). *Anal.* Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35. Found: C, 63.44; H, 5.40. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1780, 1775, 1693, 1633, 1228, 890, 825. EI-MS (m/z): 414 (M$^+$). ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

Methylfibraurin (5c)$^{1)}$——**5a** (2 g) was dissolved in 5% aqueous alkali by heating on a steam bath, and the solution was treated at room temperature with dimethylsulfate (2 ml) and then with 10% aq. NaOH. Acidification with dil. HCl and extraction with ethyl acetate afforded crystals (500 mg), which after recrystallization from MeOH, had mp 263—266 °C. *Anal.* Calcd for $C_{21}H_{22}O_7$: C, 65.27; H, 5.74. Found: C, 65.12; H, 5.67. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1763, 1698, 1630, 888, 878, 828, 817. EI-MS (m/z): 386 (M$^+$). ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

6-Hydroxyfibraurin (5d)$^{1)}$——mp 295—304 °C (dec.), colorless plates from MeOH, $[\alpha]_D^{20}$ +26.3° (pyridine, c= 0.5). *Anal.* Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.87; H, 5.24. UV $\lambda_{\max}^{\text{EtOH}}$ nm: 212, 230. FD-MS (m/z): 388 (M$^+$), EI-MS (m/z): 389 (M$^+$ + 1). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3300, 1782, 1698, 1639, 1507, 873, 810. ^{1}H-NMR as given in Table I. ^{13}C-NMR as given in Table II.

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