Structures of Lignans of *Magnolia fargesii*

Hiroshi KAKISAWA, Takenori KUSUMI,* Hong-Yen HSŪ and Yuh Pan CHEN**

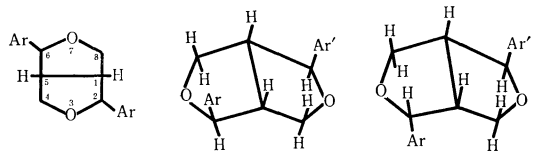
* *Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo*
** *Bristol Research Institute of Taiwan, Taipei, Taiwan*

(Received August 7, 1970)

Alcoholic extract of flower buds of *Magnolia fargesii* afforded four kinds of lignans besides some alkaloids. Two of the neutral compounds were known lignans, eudesmin (**1**), $C_{22}H_{26}O_6$, and lirioresinol-B dimethyl ether (**2**), $C_{24}H_{30}O_8$, while the remaining two were new lignans designated as magnolin and fargesin.

Magnolin, $C_{23}H_{28}O_7$, mp 97°C, ν^{KBr} 1590, 1520 cm^{-1}, $[\alpha]_D$ +55.7°, λ_{max} 231, 279 mμ, and fargesin, $C_{21}H_{22}O_6$, mp 139°C, ν^{KBr} 1605, 1590, 1505 cm^{-1}, λ_{max} 233, 284 mμ, have all their oxygen atoms in ether linkages because the IR spectra of both compounds did not show hydroxyl or carbonyl absorption. The NMR spectra (Table 1.) of both compounds are best interpreted on the basis of the skeleton of 2,6-diphenyl-3,7-dioxabicyclo[3.3.0]octane, and the structures (**3**) and (**4**) were assigned for magnolin and fargesin, respectively. These structures were supported by mass spectra.[1] The mass spectrum of magnolin (**3**) is composed of two series of fragmentation, one of which is the same as the spectrum of eudesmin (**1**), and the other lirioresinol-B dimethyl ether (**2**). Simple addition of the mass spectra of **1** and **2** led to a composite almost identical with the spectrum of magnolin. The mass spectrum of fargesin (**4**) was in a similar situation and in good agreement with the composite of the spectra of **1** and sesamin.

All six aliphatic protons attached to carbon atoms bearing the ethereal oxygens in the hydrofuran rings of magnolin appear at a lower field than δ 3.8 ppm in the NMR spectrum. Birch *et al.*[2] reported that *endo* aryl group bonded at C-2 of 3,7-dioxabicyclo[3.3.0]octane system is held very close to the *endo* hydrogen atom (8-H) on the opposite ring, which causes a high field shift (δ 3.1—3.5 ppm) of the hydrogen from the normal position (δ 3.8—4.0 ppm) by the anisotropic effect of the aryl group. These NMR features show that two aryl groups of magnolin are in the *exo* positions, and thus their stereochemistry is assigned to **3**. In contrast with magnolin, all aliphatic protons attached to the hydrofuran skelton of fargesin appeared in different positions and one of C_4-methylene protons is found at upfield (δ 3.25—3.45 ppm). Thus *endo*-C_4-hydrogen is within a shielding cone of the aryl group, which must be held at *endo* position of the opposite ring. These NMR properties are very similar to those of epieudesmin as shown in the table, and the stereochemistry of fargesin is assigned to **4**.



(**1**), (**2**) (**3**) (**4**)

(**1**) Ar=3,4-dimethoxyphenyl
(**2**) Ar=3,4,5-Trimethoxyphenyl
(**3**) Ar=3,4-dimethoxyphenyl
Ar′=3,4,5-trimethoxyphenyl
(**4**) Ar,Ar′=3,4-dimethoxyphenyl, 3,4-methylenedioxyphenyl

TABLE 1. NMR SPECTRA OF MAGNOLIN, FARGESIN, EUDESMIN AND EPIEUDESMIN

Protons	Magnolin (**3**)	Fargesin (**4**)	Eudesmin (**1**)	Epieudesmin
1-H	3.15 m	2.9 m	3.15 m	2.9 m
5-H		3.35 m		3.3 m
2-H	4.8 d(4)	4.88 d(5)	4.75 d(4)	4.85 d(5.5)
6-H		4.45 d(7)		4.45 d(7)
4-H	4.2—4.5 m (2H)	3.25—3.45 m	3.8—4.0 m (2H)	3.25—3.45 m
		3.7—4.0 m (2H)		3.7—3.9 m (2H)
8-H	3.8—4.0 m (2H)	4.1—4.25 m	4.2—4.4 m (2H)	4.1—4.4 m
OCH_3	3.85, 3.90	3.90	3.86, 3.88	3.87, 3.90
$-OCH_2O-$		5.95		
Aromatic	6.61, 6.90	6.8—6.95	6.8—7.0	6.9—7.1

1) A. Pelter, *J. Chem. Soc., C*, **1967**, 1376.

2) A. J. Birch, P. L. Macdonald and A. Pelter, *ibid.*, **1967**, 1968.