NMR Assignments of Two Furofuran Lignans from Sesame Seeds

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Two furofuran lignans, sesamolin and sesangolin were isolated from the seeds of *Sesamum indicum* and *S. angolense*, respectively. Detailed analysis of the ^{1}H- and ^{13}C-NMR spectra of these lignans was carried out by the application of two-dimensional ^{1}H-^{1}H COSY and ^{1}H-^{13}C multiple-bond, multiple-quantum spectroscopic correlation techniques.

Key words : *Sesamum indicum, S. angolense*, Pedaliaceae, furofuran lignans, NMR assignments, ^{1}H-^{1}H COSY, HMQC, HMBC

INTRODUCTION

The cultivated oilseed crop, *Sesamum indicum* L. (Pedaliaceae) is known to contain variable amounts of the furofuran lignans sesamin and sesamolin in its seed oil (Ryu *et al.*, 1992; Kamal-Eldin and Appelqvist, 1994). Another related lignan sesangolin was isolated from the wild type sesame plant, *S. angolense* Welw. (Jones *et al.*, 1962; Ryu *et al.*, 1993). These sesamin type lignans are known for their strong antioxidative activities (Osawa, 1992). The structures of these lignans are well established (Haslam, 1970; Jones *et al.*, 1962) as shown in Fig. 1, but the ^{13}C-NMR assignments for sesamolin (**1**) and sesangolin (**2**) are not fully characterized so far. In this paper, we report the NMR assignments of these compounds which were made with the aid of 2D correlation NMR techniques such as HMQC and HMBC.

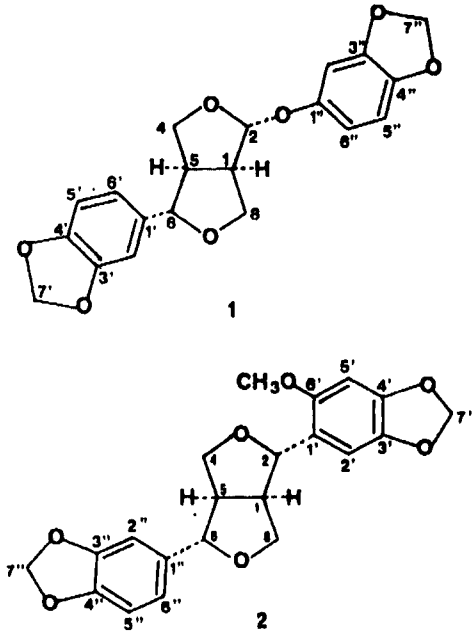

Fig. 1. Structures of sesamolin (1) and sesangolin (2).

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MATERIALS AND METHODS

The general experimental methods are the same as those reported in Kang *et al.* (1994). Sesamolin (**1**) and sesangolin (**2**) were isolated from the seeds of *S. indicum* and *S. angolense*, respectively, as described in Ryu *et al.* (1992; 1993) and identified by direct comparison with authentic samples (mmp, UV, IR, NMR and MS).

RESULTS AND DISCUSSION

The ^{1}H-NMR chemical shifts of **1** was previously reported (Haslam, 1970) which were indistinguishable from those of our results as tabulated in Table I. The proton chemical shifts of **2** could be assigned in detail compared to data reported for similar and related compounds (Pelter *et al.*, 1976; Nagata *et al.*, 1987) as well as based on the ^{1}H-^{1}H COSY spectra. It showed a multiple signal assigned to one methine proton at δ 2.94 (H-1), which was found to be coupled with a benzylic proton at δ 5.04 (d, H-2) and also with a pair of methylene protons at δ 4.30 and 4.01 (H-8) through ^{1}H-^{1}H COSY-45 and HMQC experiments. In

Table I. Chemical shifts and correlations of sesamolin (**1**) in $CDCl_3$

Position	δ_H	δ_C	HMBC
C-1	3.30 (q, 8.5)	53.2	
C-2	5.49 (s)	106.8	C4, C5, C8
C-4	4.12 (dd, 8.5, 9.1)	69.7	C1, C2, C6
	3.96 (d, 9.1)		
C-5	2.94 (q, 8.5)	52.7	
C-6	4.39 (d, 8.5)	87.0	
C-8	4.43 (t, 9.0)	71.2	C2, C6
	3.63 (dd, 8.5, 9.0)		
C-1'		134.3	
C-2'	6.87 (d, 1.2)	106.5	C4', C6'
C-3'		148.0	
C-4'		147.3	
C-5'	6.78 (d, 7.8)	108.1	C1', C3'
C-6'	6.82 (dd, 1.2, 7.8)	119.6	C2', C4'
C-7'	5.91	101.2	C3'
C-1"		151.8	
C-2"	6.62 (d, 2.5)	100.1	C4"
C-3"		148.1	
C-4"		142.6	
C-5"	6.70 (d, 8.5)	108.0	C1", C3"
C-6"	6.50 (dd, 2.5, 8.5)	108.9	C2", C4"
C-7"	5.95 (s)	101.0	C3"

Coupling constants (J in Hz) in parentheses.

Table II. Chemical shifts and correlations of sesangolin (**2**) in $CDCl_3$

Position	δ_H	δ_C	HMBC
C-1	2.94 (m)	54.6	
C-2	5.04 (d, 4.2)	82.0	C4, C8, C1', C2'
C-4	4.20 (dd, 6.1, 8.8)	71.4	C1, C2, C6
	3.91 (dd, 3.4, 8.8)		
C-5	2.93 (m)	54.3	
C-6	4.66 (d, 5.2)	85.3	C4, C5", C6"
C-8	4.30 (dd, 7.1, 9.0)	73.1	C2, C5, C6
	4.01 (dd, 3.8, 9.0)		
C-1'		123.1	
C-2'	6.90 (s)	105.8	C4', C6'
C-3'		141.1	
C-4'		147.1	
C-5'	6.52 (s)	94.5	C1', C3', C4'
C-6'		151.4	
C-7'	5.91 (d, 1.5)	101.0*	C3', C4'
	5.90 (d, 1.5)		
OCH_3	3.77 (s)	56.2	C6'
C-1"		135.3	
C-2"	6.86 (d, 1.5)	106.5	C4", C6"
C-3"		147.9	
C-4"		147.1	
C-5"	6.77 (d, 7.6)	108.1	C1", C3"
C-6"	6.81 (dd, 1.5, 7.6)	119.4	C2", C4"
C-7"	5.94 (s)	101.1*	C3"

*Assignment may be reversed. Coupling constants (J in Hz) in parentheses.

a similar manner, another multiplet proton at δ 2.93 (H-5) was coupled with another pair of methylene protons at δ 4.20 and 3.91 (H-4), and another benzylic proton at δ 4.66 (H-6). These signals supported the presence of unsymatrically substituted 2,6-diaryl *cis*-3,7-dioxabicyclo[3.3.0]octane in **2** (Pelter *et al.*, 1976). The proton signals attributable to the 3,4-methylenedioxy-6-methoxyphenyl and piperonyl (3,4-methylenedioxyphenyl) moieties in **2** were assigned as follows. The two singlet signals at δ 6.90 and 6.52 ppm were shown to be correlated with methylenedioxy doublet protons (J=1.5 Hz) at δ 5.90 and 5.91 ppm, which permitted that these protons were discernible from those for 3,4-methylenedioxyphenyl residue in **2**. The presence of long-range couplings between H-2 and one of singlet signals at δ 6.90, and between a methoxy signal at δ 3.77 and a singlet signal at δ 6.52 ppm allowed the assignments of the signals at δ 6.90 and 6.52 ppm ascribable to H-2' and H-5', respectively in 3,4-methylenedioxy-6-methoxyphenyl moiety in **2**. The assignments of protons in piperonyl moiety were easily made with the aid of the coupling constants. Two doublets for one of each *o*- and *m*-coupled proton at δ 6.77 (J=7.6 Hz) for H-5" and δ 6.86 (J=1.5 Hz) for H-2", respectively, and double doublets at δ 6.81 (J=1.5, 7.6 Hz) for H-6" were observed. The H-2" and H-6" protons were long-range coupled with H-6 proton at δ 4.66 ppm. On the basis of the above results, the proton chemical shifts for **2** were assigned as shown in Table II.

^{13}C-NMR spectroscopy has proved to be a valuable technique for solving the problems of structure and stereochemistry in the furofuran lignans. Thus, the aromatic resonances C-1' and C-1" are dependant on the configuration, as well as on the nature of the substituents on the aryl ring, but carbons 1, 2, 8, 4, 5 and 6 are affected by the stereochemistry only (Pelter *et al.*, 1976; Agrawal and Thakur, 1985). The ^{13}C chemical shifts of furofuran ring in **2** except for C-2 and 8 agreed well with previously reported data (Agrawal and Thakur, 1985; Ina *et al.*, 1987; Miyazawa *et al.*, 1994), but C-2 and 8 chemical shifts were resonated at δ 82.0 and 73.1 ppm, respectively, as can be seen in sesaminol glucosides (Katsuzaki *et al.*, 1994). However, the ^{13}C chemical shifts of furofuran ring in **1** were somewhat different from those of 2,6-diaryl furofuran lignans due to aryloxy substituent at C-2 position, but assignment of each carbon could be determined on the basis of HMQC and HMBC experiments. The carbon chemical shifts for piperonyl moieties in **1** and **2** could be straightforwardly assigned with the aid of DEPT and HMQC experiments as well as comparing the literature data for sesamin analogues. The resonances for C-1' in 1 and C-1" in 2 at δ 134.3 and 135.3, respectively follow the literature data and are associated with equatorial piperonyl group (Pelter *et al.*, 1977). The chemical shifts corresponding to 3,4-methylenedioxyphenoxy residue in **1** and 3,4-methylenedioxy-6-methoxyphenyl moiety

in **2** could be assigned in a similar manner. The above assignments were further confirmed by HMBC experiments as indicated in Tables I and II.

REFERENCES CITED

Agrawal, P.K. and Thakur, R.S., ^{13}C NMR Spectroscopy of Lignan and Neolignan Derivatives, *Magn. Reson. Chem.*, 23, 389-418 (1985).

Haslam, E., The Stereochemistry of Sesamolin, *J. Chem. Soc.(C)*, 2332-2334 (1970).

Ina, H., Asai, A., Iida, H. and Ushida, T., Chemical Investigation of *Hydrocotyle sibthorpioides, Planta Med.*, 53, 228(1987).

Jones, W.A., Beroza, M. and Becker, E.D., Isolation and Structure of Sesangolin, a Constituent of *Sesamum angolense* (Welw.), *J. Org. Chem.*, 27, 3232-3235 (1962).

Kamal-Eldin, A. and Appelqvist, L.A., Vriations in the Composition of Sterols, Tocopherols and Lignans in Seed Oils from Four *Sesamum* Species, *J. Am. Oil Chem. Soc.*, 71, 149-156 (1994).

Kang, S.S., Lee, E.B., Kim, T.H., Kim, K.R. and Jung, J. H., The NMR Assignments of Torilin from *Torilis japonica, Arch. Pharm. Res.*, 17, 284-286 (1994).

Katsuzaki, H., Kawakishi, S. and Osawa, T., Sesaminol Glucosides in Sesame Seeds, *Phytochemistry*, 35, 773-776 (1994).

Miyazawa, M., Ishikawa, Y., Kasahara, H., Yamanaka, J.-I. and Kameoka, H., An Insect Growth Inhibitory Lignan from Flower Buds of *Magnolia fargesii, Phytochemistry*, 35, 611-613 (1994).

Nagata, M., Osawa, T, Namiki, M., Fukuda, Y. and Ozaki, T., Stereochemical Structures of Antioxidative Bisepoxylignans, Sesaminol and Its Isomers, Transformed from Sesamolin, *Agric. Biol. Chem.*, 51, 1285-1289 (1987).

Osawa, T., Phenolic Antioxidants in Dietary Plants as Antimutagens: In Huang, M.-T., Ho, C.-T and Lee, C.Y.(Eds.), *Phenolic Compounds in Food and Their Effects on Health II*, American Chemical Society, Washington, DC, 1992, pp. 135-149

Pelter, A., Ward, R.S., Rao, E.V. and Sastry, K.V., Revised Structures for Pluviatilol, Methyl Pluviatilol and Xanthoxylol, *Tetrahedron*, 32 2783-2788 (1976).

Pelter, A., Ward, R.S. and Nishino, C., Revised Structures for Epiaschantin and Epimagnolin, *Tetrahedron Lett.*, 4137-4140 (1977).

Ryu, S.R., Lee, J.I., Kang, S.S. and Choi, C.Y., Quantitative Analysis of Antioxidants in Sesame Seed, *Korean J. Crop Sci.*, 37, 377-382 (1992).

Ryu, S.R., Kang, S.S., Lee, J.I. and Choi, C.Y., Isolation and Quantitative Analysis of Sesangolin in Wild Sesame, *Korean J. Breed.*, 25, 55-58 (1993).