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Isolation and Characterisation of a New Stereoisomeric Furofuran Type of Lignan from *Ecbolium linneanum* Kurz.

R. VENKATARAMAN† and S. GOPALAKRISHNAN*
Department of Chemistry, Manonmaniam Sundaranar University
Abishekapatti, Tirunelveli-627 012, Tamil Nadu, India
e-mail: msunet@md2.vsnl.net.in

A new streoisomeric furofuran type of lignan was isolated from the petroleum ether (40–60°C) extract of the root of *Ecbolium linneanum* Kurz. (Acanthaceae). The structure was elucidated by spectroscopic methods as 2-(2-methoxy-3,4-methylenedioxyphenyl)-6-(2-methoxy-3,4-methylene dioxyphenyl)-3,7-dioxabicyclo [3.3.0]-octane and named as Ecbolin B.

Key words: Isolation, characterisation, lignan, *Ecbolium linneanum* Kurz.

INTRODUCTION

Ecbolium linneanum Kurz. (Fam. Acanthaceae), a low shrub commonly called 'Nilambari' in Tamil and 'Udajati' in Sanskrit is distributed in Western Ghats of India.[1] The roots are traditionally used in jaundice, menorrhoea and tumour.[2–4] Nair *et al.*[5] have isolated orientin, vitexin and their isoflavones from *E. linneanum*. In our previous work on the root of *E. linneanum*, a new unsymmetrical furofuran type of lignan called Ecbolin A has been isolated from the chloroform extract and characterised by spectroscopic and X-ray studies[6]. In this communication, the isolation and characterisation of another new streoisomeric furofuran type of lignan, named as Ecbolin B, has been presented. Since lignans are known to have antitumour, antimitiotic and antiviral activities and the compounds containing methylene dioxy group are reported[7] to be useful in jaundice, the biological activities of Ecbolin B are under investigation.

EXPERIMENTAL

The root of *E. linneanum* Kurz. (Fam. Acanthaceae) was collected from Courtallam Hills of Western Ghats of South India in the month of January and identified by Dr. V. Chelladurai, Research Officer (Botany), Survey of Medicinal Plants Unit-Siddha, CCRAS, Palayamkottai-627 002, Tamil Nadu, India. Voucher specimen (Voucher No. MSU0021) was deposited at the Herbarium, Department

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†*Present address*: Department of Chemistry, Sri Paramakalyani College, Alwarkurichi-627 412, Tamil Nadu, India.

of Chemistry, Manonmaniam Sundaranar University, Tirunelveli-627 012, Tamil Nadu, India. Air-dried roots of *E. linneanum* (200 g) were extracted in petroleum ether (40–60°C) in a Soxhlet apparatus. The extract upon concentration yielded colourless amorphous solid (50 mg). It was recrystallised with petroleum ether (40–60°C). It was found to be single in TLC ($R_f = 0.14$) in benzene : chloroform (9 : 1) and was named as Ecbolin B.

Ecbolin B was obtained as colourless needles, m.p. 94°C; EIMS ms m/z 414 (80) $[M]^{+\bullet}$, 383 (21), 191 (73), 179 (100), 165 (69), 152 (38). HREIMS: m/z 414.02 (Calcd. for $C_{22}H_{22}O_8$). UV λ_{max}^{MeOH} 237 nm; IR $\bar{v}_{max}^{MeOH}$, 1620, 1460, 1200, 1102, 1020 cm^{-1}; ^{1}H-NMR and ^{13}C-NMR ($CDCl_3$, 400 MHz (Tables 1 and 2).

RESULTS AND DISCUSSION

The high resolution electron impact mass spectra of Ecbolin B indicating the molecular weight of 414.02 corresponds to the m.f. $C_{22}H_{22}O_8$. The UV spectrum of Ecbolin B showed a maximum at 237 nm indicating furofuran type of lignan.[8] IR spectrum of the compound taken in $CHCl_3$ exhibited bands at 1620, 1460, 1200, 1102, 1020 cm^{-1}. The peak at 1102 cm^{-1} corresponds to O—C—O stretching. Aromatic C—H stretching frequency appeared at 1460 cm^{-1}. No peak at 3500 cm^{-1} indicated the absence of free hydroxy groups in the compound. ^{1}H-NMR signal pattern in aromatic region was strongly suggesting the presence of *ortho*-coupled protons at 6.85 δ and 6.50 δ. It also showed signals at 4.00 δ indicating the presence of one methoxyl group in each aromatic ring. The peak at 5.91 δ corresponds to —O—CH_2—O— groups. ^{13}C-NMR signals at 102.3, 118.6, 127.5, 136.4, 140.8, 148.8 were assigned for aryl carbon atom of the ring. The methylene dioxy group was assigned with 101.0 δ. The methoxyl group was assigned with 59.4 δ (Tables 1 and 2). Both ^{1}H-NMR and ^{13}C-NMR values were in good agreement with symmetrically substituted furofuran type of lignans reported earlier.[8–12] On the basis of UV, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectral

TABLE 1
^{1}H-NMR DATA OF ECBOLIN B AND ITS CLOSELY RELATED COMPOUNDS

Hydrogen atoms	Episesamin* (δ)	Eudesmin* (δ)	2′,2″-dimethoxy sesamin† (δ)	Ecbolin B (δ)
1,5	3.15 (m)	3.15 (m)	2.93 (ddd)	2.93 (m)
2,6	435 (d, J = 7.5Hz) 4.76 (d = 5.0 Hz)	4.75 (d, J = 4.0 Hz)	4.99 (d)	4.99 (d, J = 3.9 Hz)
4,8	3.6–4.15 (m) 3.6–4.15 (m)	3.8–4.0 (m) 4.2–4.4 (m)	4.03 (dd) 4.25 (dd)	4.01 (m) 4.25 (t, J = 7.8 Hz)
5′,5″	—	—	6.50 (d)	6.50 (d, J = 8.0 Hz)
6′,6″	—	—	6.85 (d)	6.85 (d, J = 8.0 Hz)
—OCH_3	—	3.86, 3.90 (3H, s)	4.01 (s)	4.00 (3H, s)
—OCH_2O—	5.87 (2H, s)	—	5.92 (ABq)	5.91 (2H, s)

*Pelter *et al.*[12], 1978. †Jaensch *et al.*[9], 1989.

data, the compound was considered to be 2-(2-methoxy-3,4-methylene dioxyphenyl)-6-(2-methoxy-3,4-methylene dioxyphenyl)-3,7-dioxabicyclo[3.3.0] octane and named as Ecbolin B(1). The structure for Ecbolin B was also confirmed by ^{1}H-^{1}H-COSY, ^{1}H-^{13}C-COSY and COLOC spectral data for the first time in the present investigation.

TABLE 2

^{13}C-NMR SPECTRAL DATA OF ECBOLIN B AND ITS RELATED COMPOUNDS

Carbon atom	Sesamin* (ppm)	Epiesamin* (ppm)	Ecbolin B (ppm)
1	54.2	54.7	54.3
2	85.6	87.7	81.8
4	71.5	71.04	72.7
5	54.2	50.2	54.3
6	85.6	82.1	81.8
8	71.5	69.7	72.7
1′	134.9	135.6	127.5
2′	106.3	106.6	140.8
3′	146.8	146.8	136.4
4′	147.7	147.9	148.8
5′	107.9	108.8	102.3
6′	119.1	118.8	118.6
1″	134.9	132.6	127.5
2″	106.3	106.7	140.8
3″	146.8	147.4	136.4
4″	147.7	148.2	148.8
5″	107.9	108.2	102.3
6″	119.1	119.6	118.6
—OCH_2O—	100.89	101.14	101.0
—OCH_3	—	—	59.4

*Pelter *et al*[12].

The various ^{1}H-^{1}H-COSY correlations of Ecbolin B are the following:

6.50 δ is correlating with 6.85 δ
4.99 δ is correlating with 2.93 δ
4.25 δ is correlating with 4.01 δ

The various ^{1}H-^{13}C-COSY correlations of Ecbolin B are the following:

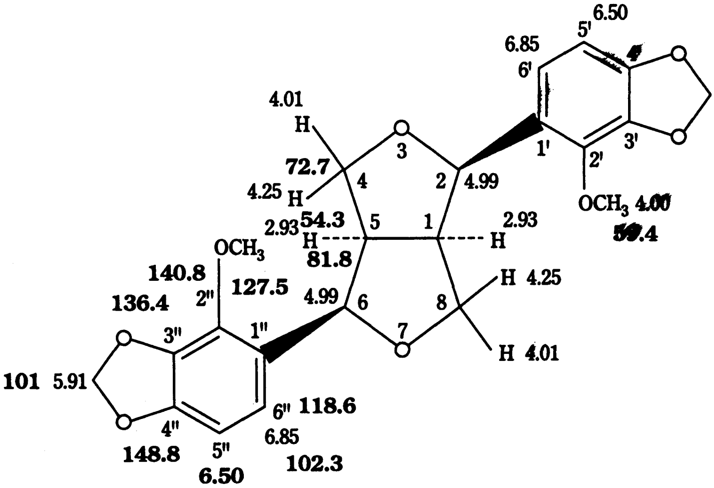
2.93 δ is correlating with 54.3 ppm
4.99 δ is correlating with 81.8 ppm
4.01 δ is correlating with 72.7 ppm
4.25 δ is correlating with 72.7 ppm

5.91 δ is correlating with 101.0 ppm
4.00 δ is correlating with 59.4 ppm
6.50 δ is correlating with 102.3 ppm
6.85 δ is correlating with 118.6 ppm

The various COLOC correlations of Ecbolin B are the following:

6.85 δ is correlating with 148.8 ppm
6.85 δ is correlating with 140.8 ppm
6.50 δ is correlating with 136.4 ppm

These assignments are indicated in structure (1).



Note: The values in bold print refer to carbon atoms.
The values in normal print refers to hydrogen atoms.

Past work indicated[9] that Ecbolin B must be a streoisomer of 2′,2″-dimethoxysesamin. Comparison of melting points of various streoisomeric symmetrically substituted 2,6-diaryl-3,7-dioxabicyclo-[3.3.0]-octane type of compounds revealed the fact that the diequatorial isomer showed the lowest melting point, the diaxial isomer showed the highest melting point and the axial-equatorial isomer showed melting point in between that of diaxial and diequatorial isomer[12] (Table-3).

2′,2″-Dimethoxysesamin was reported[9] to be a colourless liquid. However, Ecbolin B is a sharp melting solid (m.p. 94°C). Hence Ecbolin B must be a diaxial isomer of 2′,2″-dimethoxysesamin. This is also supported by ^{13}C-NMR shift values of carbon atoms reported[12] earlier for episesamin. ^{13}C-NMR shift values of carbon atoms 1′ and 1″ in particular are characterestic of streochemistry of attachment of the diaxial-3,4-methylene dioxyphenyl group in 2,6-diaryl-3,7-dioxabicyclo-[3.3.0]-octane. ^{13}C-NMR shift values of 1′,1″ carbon atoms of equatorial-3,4-methylene dioxyphenyl group of episesamin come at 134.93–135.63 ppm whereas that of axial-3,4-methylene dioxyphenyl group of episesamin appears at 132.65 ppm. These criteria can therefore be used to establish the stereochemistry of both aryl groups in the molecule. In Ecbolin B, the lowest value of 127.5 ppm for both 1′ and 1″ carbon atoms of 3,4-methylene dioxyphenyl groups strongly favoured the diaxial conformation. Hence Ecbolin B must be considered as a new stereoisomer of symmetrically substituted furofuran type (1).

TABLE 3
MELTING POINTS (°C) OF SYMMETRICALLY SUBSTITUTED FUROFURAN TYPE LIGNANS

Name of the compound	Nature of aryl attachment to furofuran skeleton	m.p. (°C)
Sesamin	Diequatorial	123
Episesamin	Axial-equatorial	121–125
Diasesamin	Diaxial	168–171
Pinoresinol	Diequatorial	120–121
Epipinoresinol	Axial-equatorial	137–138
Eudesmin	Diequatorial	107
Epieudesmin	Axial-equatorial	125–126
Diaeudesmin	Diaxial	157–158
Syringaresinol	Diequatorial	172–177
Episyringaresinol	Axial-equatorial	210–211
Yangamin	Diequatorial	121–123
Epiyangamin	Axial-equatorial	118–120
Diayangamin	Diaxial	151–152
Excelsin	Diequatorial	122–123
Epiexcelsin	Axial-equatorial	164.5–165.5

*Pelter *et al.*[12]

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