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Structural characterization of a new compound from *Strobilanthes ciliatus* Nees.

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ABSTRACT

Strobilanthes ciliatus is one of the species endemic to Western Ghats, India. Chemical constituents of *Strobilanthes ciliatus* were investigated by means of chromatographic techniques. A new compound 4-Acetyl-2, 7-dihydroxy-1, 4, 8-triphenyl-octane-3, 5-dione was isolated. The structure was elucidated on the basis of spectral data (IR, MS and NMR), mainly 1D and 2D NMR data.

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KEYWORDS

Strobilanthes ciliatus;
Acanthaceae;
Structure elucidation;
Natural product;
NMR.

INTRODUCTION

Strobilanthes is one of the most interesting genera in the family Acanthaceae known for its diversified habits, gregarious nature and infrequent but elegant flowering. This is the second largest genus in the family with approximately 300 species entirely restricted to hills in tropical Asia. The Indian subcontinent has nearly 150 species out of which 59 are seen in peninsular India. The genus is not greatly explored for economic utility. Out of the 59 species of *Strobilanthes* seen in south India 39 are endemic to peninsular India. *Strobilanthes ciliatus* is one of the species endemic to Western Ghats, India. This plant has got several therapeutic properties. *Strobilanthes ciliatus* has a strong aroma and is used medicinally. It is widely used in Ayurveda as a source of the drug 'Sahachara'^[1]. The plant is used for a variety of ailments like rheumatism, lumbago, sciatica, limping, chest congestion, strangury, fever, leucoderma, skin diseases, inflammations, cough, bronchitis, odontalgia and general debility^[2].

The review of literature shows that only very few species in the genus *Strobilanthes* has been investigated for their chemical constituents. One of species *Strobilanthes cusia* was found to be a good source of tryptanthrin^[3]. Several triterpenoids mainly lupeol, betulin, lupenone from various species of *Strobilanthes*. The genus *Strobilanthes* is found to a good source of flavanoids and lignans. The important lignans isolated from this genus are (+) lyoniresinol 3-O-β-D-apiofuranosyl-(1-2)-β-D-glucopyranoside and two phenylethanoid glycoside [2, (3,4-dihydroxyphenylethyl)]-3-O-α-D-apiofuranosyl-(1-4)-4-O-caffeoyl-β-D-glucopyranoside (cusianoside A) and [2, (3,4-dihydroxyphenylethyl)]-3-O-β-D-xylopyranosyl-(1-3)-4-O-caffeoyl-β-D-glucopyranoside (cusianoside B), (+)-5,5'-dimethoxy-9-O-β-D-glucopyranosyl larciresinol, (+)-9-O-β-D-glucopyranosyl lyoniresinol, (+)-5,5'-dimethoxy-9-O-β-D-glucopyranosyl secoisolarciresinol and acetoside from *Strobilanthes cusia*^[4]. In this paper we report the isolation characterization of a dione from

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dimethoxy-9-O- β -D-glucopyranosyl secoisolariciresinol and acetoside from *Strobilanthes cusia*^[4]. In this paper we report the isolation characterization of a dione from *Strobilanthes ciliatus*.

EXPERIMENTAL

Strobilanthes ciliatus stems (2 Kg) was collected from the reserve forests of Nilambur, Malappuram District, Kerala State, India in the month of May 2007. Air dried pieces of stems were thoroughly percolated separately and extracted with petroleum ether (60^o-80^o C) for 12 hours and the residual plant material was then extracted with acetone (2.5 L) for a period of (2 x 12) hours. The acetone extract (20g) was then subjected to column chromatography over silicagel and eluted with petroleum ether containing increasing percentages of ethyl acetate. Fractions eluted with 100 percentage petroleum ether yielded compound 1 (1.2 g), fractions eluted with 49:1 petroleum ether: ethyl acetate yielded compound 2 (500mg), fractions eluted with 19:1 petroleum ether: ethyl acetate yielded compound 3 (300mg), fractions eluted with 4:1 petroleum ether: ethyl acetate yielded compound 4 (20 mg) and fractions eluted with 1:1 petroleum ether: ethyl acetate yielded compound 5 (350 mg).

Melting points were measured on electrical melting point apparatus (Joshiba) and were uncorrected. Infrared (IR) spectra were recorded on Shimadzu FT-IR (4000-400) spectrophotometer. Mass spectra were recorded in GC-8000^{TOP} CE instrument. ¹H, ¹³C-NMR and DEPT spectra were recorded on Bruker Advance 400 Spectrometer. Deuterated chloroform (CDCl₃) was used as solvent. Acme silica gel of 60-120 mesh activated at 120^oC was used as adsorbent in column chromatography. Silica gel (100 mesh) with 13% CaSO₄ ½ H₂O binder was used as solid stationary phase in thin layer chromatography. The spots were visualized under UV light at wavelength 254 nm and 365 nm and in iodine vapours.

RESULTS AND DISCUSSION

Compound 1, 2, 3 and 5 have been characterized as lupeol, stigmasterol, betulin, stigmasterol glycoside

and their isolation has been reported in our previous paper^[5].

Compound 4 was isolated as a white powder with melting point 170^oC. The mass spectrum of compound 4 showed the molecular ion peak at m/z 444 corresponding to the molecular formula C₂₈H₂₈O₅. The spectrum of compound 4 showed characteristic absorption for hydroxyl group at 3313 and 1031. The characteristic absorption for the presence of carbonyl (C=O) grouping is also seen at 1726, 1660 and 1631 cm⁻¹. The ¹H NMR and ¹³C NMR spectral data are given in TABLE.1 and 2 respectively. The ¹H NMR showed a sharp singlet at 2.039(1H, s) indicating the presence of an acetoxy group in the compound. The ¹H NMR showed the presence of 8 aliphatic protons and 15 aromatic protons. The aliphatic protons were seen as two pairs of doublets of doublets at δ 3.07 (1 H, dd, J= 8.5 Hz, 8.5 Hz), δ 3.23 (1H, dd, J=6Hz, J=6Hz), δ 3.83 (1H,dd, J=5 Hz,, J= Hz), δ 3.93 (1H J=5Hz, 5 Hz), a multiplet of 8 lines at δ 2.76 (1H), two multiplets at δ 4.35 (1H), δ 4.78 (1H). The two hydroxyl protons were observed at δ 6.01 and 6.76. The ¹H-¹H COSY spectrum showed the coupling between the methylene at δ 2.76 (m, 2H), CH at δ 4.4 (1H, m) and CH₂ at δ 3.93 (1H J=Hz) and δ 3.83 (m J= 4 Hz). One more correlation was seen between CH₂ at δ 3.23 (J=6Hz) and δ 3.07 (dd, J=8.5 Hz) with that of CH at 4.77 (m) and OH at 6.78.

The aromatic protons were seen as a doublet at δ 7.08 (2H), a multiplet at δ 7.15 (3H), a multiplet at δ 7.27 (5H), a triplet at δ 7.45 (2 H), a triplet at δ 7.5 and a doublet at δ 7.75 (1 H). From the ¹H-¹H COSY spectrum of compound 4 it was seen that the aromatic protons formed parts of three individual mono substituted benzene rings which are not coupled to each other. It was seen that the doublet at δ 7.08 (2H) and the multiplet at δ 7.15 (3 H) were coupled. This coupling indicated that doublet at δ 7.08 (2H) is due to the two ortho protons and the multiplet at δ 7.157 (3 H) is due to the two meta protons and one para proton. Another coupling interaction was shown within the multiplet at δ 7.27 integrating to 5H. This also indicated a mono substituted benzene ring. Further coupling among the aromatic protons were seen between the doublet at δ 7.75 and triplet at δ 7.45, between the triplet at δ 7.45 and triplet at δ 7.54. This correlation also clearly indicates

the coupling with ortho- para and para-meta protons respectively.

The ^{13}C NMR spectrum of compound 4 showed a total of 22 signals with 7 carbons in the aliphatic region

TABLE 1 : ^1H NMR chemical shifts of compound 4

Proton	δ	Multiplicity
H-2'', H-6''	7.721	d, 2H
H-4''	7.540	t, 1H
H-3'', H-5''	7.45	t, 2H
H-2''', H-3''', H-4''', H-5''', H-6'''	7.27	5H, M
H-2', H-4', H-6'	7.167	m, 3H
H-3', H-5'	7.091	d, 2H, 1.5 Hz
OH-2	6.78	d, 1H, 8 Hz
OH-7	6.013	d, 1H, 8.5 Hz
H-2	4.8	1H, m
H-7	4.39	1H, m
Ha-6	3.837	1H, dd, J=5 Hz, J= 5Hz
Hb-6	3.937	1H, dd, J=5Hz, 5 Hz
Ha-1	3.077	1 H, dd, J= 8.5 Hz, 8.5 Hz
Hb-1	3.237	1H, dd, J=6Hz, J=6Hz
H-8	2.793	1H, m
H-2''''	2.039	3H, s

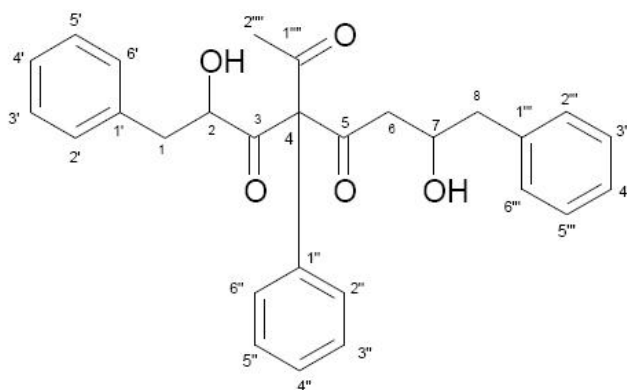
TABLE 2 : ^{13}C NMR chemical shifts of compound 4

Carbon	Multiplicity	δ	Carbon	Multiplicity	δ
1	CH ₂	38.44	4'	CH	126.03
2	CH	54.97	1''	C	133.65
3	C=O	167.10	2'', 6''	CH	127.03
4	C	29.69	3'', 5''	CH	128.56
5	C=O	170.75	4''	CH	131.90
6	CH ₂	64.57	1'''	C	136.65
7	CH	49.44	2''', 6'''	CH	129.12
8	CH ₂	37.42	3''', 5'''	CH	129.28
1'	C	136.60	4'''	CH	127.13
2', 6'	CH	128.62	1''''	C=O	170.24
3', 5'	CH	128.75	2''''	CH ₃	20.77

and 15 carbons in the aromatic region. It is seen that 6 signals at δ 127.04, 128.58, 128.64, 128.76, 129.12, and 129.28 were of double intensity as may be counted for two carbons each. This has been confirmed from the HSQC spectrum in which these six carbons were found to be correlated to the three sets of aromatic protons each. Hence it was accounted that these six carbon signals are due to the three pair of ortho and

meta protons of the three benzene rings. This finding has been supported by the integration values in the ^1H NMR which counted for a total of 15 aromatic protons. The DEPT 45 spectra showed the presence of 11 methine carbons including the two aliphatic methines at δ 49.42 and δ 54.97. The DEPT 135 spectra showed the presence of three negative signals (3 methylene) and twelve positive signals (eleven methine groups and a lone methyl group). This information supported the presence of the acetoxyl methyl at δ 2.03. Further four quaternary carbons were seen at δ 133.65, 136.60, 136.68 and 29.69; three in the aromatic region confirming the mono substitution of the benzene rings and the signal at δ 29.69 indicates an aliphatic quaternary in the compound. Also three carbonyl functional groups indicated by signals at δ 167.10, 170.24, 170.75.

The HMBC spectrum was used to ascertain the structure of compound 4 and to make a thorough as-



signment of ^1H and ^{13}C chemical presented in TABLE 1 and 2. The cross correlation of C-8 (δ 37.42) with the protons of H-2''', H-6''' (δ 7.27) was observed in the HMBC spectrum suggesting the attachment of C-8 methylene group to the aromatic carbon at C-1'''. Similar cross peaks were also observed between C-1 (δ 38.44) with the protons at H-2', H-6' (δ 7.167) revealing the attachment of the C-1 methylene to that of the aromatic carbon at C-1'. The C-1'' carbon showed cross correlation with H-2'', H-6'' (δ 7.721) and H-3'', H-5'' (7.45) protons only suggesting the presence of two quaternary carbons adjacent to C-1''. This confirms the linkage of C-1'' aromatic carbon to the quaternary carbon at C-4. The C-1'''' (δ 20.77) carbon shows correlation only with the H-2'''' (2.039) proton only confirming the presence of acetyl functionality. All

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other relevant correlations were also seen in the HMBC spectrum thus confirming the proposed structure and compound 4 has been found to be 4-Acetyl-2, 7-dihydroxy-1, 4, 8-triphenyl-octane-3, 5-dione.

CONCLUSION

Phytochemical analysis of *Strobilanthes ciliatus* has led to the isolation of a new dione along with lupeol, stigmaterol, betulin and stigmaterol glycoside. Isolation and purification of other fractions of this plant is being carried out. Some of these fractions contain terpenoids and lignans that may have new structures. This present work brings significant phytochemical results, contributing to the scientific advancement of this widely used medicinal species *Strobilanthes ciliatus*.

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