Journal of Scientific and Innovative Research 2013; 2 (4): 777-784
Available online at: www.jsirjournal.com

Research Article

ISSN 2320-4818
JSIR 2013; 2(4): 777-784

Received: 18-08-2013
Accepted: 29-09-2013

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Isolation of a novel terpenoid from the rhizome of *Curcuma caesia* Roxb.

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Abstract

Isolation and characterisation of a novel terpenoid from the rhizome of *Curcuma caesia* Roxb. (Black turmeric) followed by assessment of its bioactivity. Chemical characterisation of the sample was done through UV, IR (FT-IR), HRMS and NMR spectroscopic techniques. The sample was identified as (2Z,2'Z)- 2,2'-(3aR,10aS)- 1,3,5,8,9,9- hexamethyl-1,2,3,3a-tetrahydrobenzo [f] azulene-4,10 (5H,8H,9H,10aH)- diylidene) diacetaldehyde. This study is probably the first report of presence of (2Z,2'Z)-2,2'- (3aR,10aS)- 1,3,5,8,9,9- hexamethyl-1,2,3,3a- tetrahydrobenzo [f] azulene- 4,10 (5H,8H,9H,10aH)- diylidene) diacetaldehyde in plants.

Keywords: *Curcuma caesia* Roxb., (2Z,2'Z)-2,2'- (3aR,10aS)-1,3,5,8,9,9- hexamethyl-1,2,3,3a-tetrahydrobenzo [f] azulene- 4,10 (5H,8H,9H,10aH) -diylidene) diacetaldehyde, Physiochemical characterisation, Isolation.

Introduction

Curcuma caesia Roxb. (Black turmeric) of the family Zingeberaceae is an important unexplored plant valued all over the Asia for its medicinal properties. Black turmeric is an uncommon endemic as well as ethnomedicinally important of South East Asia. It is a natural triploid plant and has a reduced growth rate. Black turmeric powder is utilised by several tribals of the district Nadia of West Bengal, India to incerase the mucus content in gastric juices, to treat fevers, stomach problems, allergies, diarrhea, chronic cough, heartburn, wind, bloating, colic, bronchial asthma, flatulence, and jaundice and other liver ailments. Externally, it has been used for reducing inflammation and swelling due to sprains, cuts, and bruises. So far eight natural products have been isolated and characterised from Curcuma caesia Roxb. like Borneol, Borneol acetate, 1,8-Cineole, α-Curcumene, γ-Curcumene, β-Elemene, (E)-β-Ocimene, ar-Turmerone etc. [1, 2]. Here we report for the first time the presence of (2Z,2'Z)-2,2'- (3aR,10aS)-1,3,5,8,9,9-hexamethyl- 1,2,3,3a -tetrahydrobenzo [f] azulene- 4, 10 (5H,8H,9H,10aH)-diylidene) diacetaldehyde compound form the plant *Curcuma caesia* Roxb. As per thorough literature survey this compound have seem to be a novel one which was not reported earlier.

Materials and methods

Collection of Plant Material

Whole plant of *C. caesia* was collected in the month of July 2010 from experimental garden of Department of Botany, University of Kalyani, and was identified in the Department of Botany, University of Kalyani, Nadia, West Bengal, India.

Extraction and Isolation of Crude Secondary Metabolite Content

2.5 kg shade dried rhizomes of black turmeric plant was powdered of approximately and extracted three times with 1 liter of 95% EtOH at room temperature to give an extract of 479 gms. The extract was evaporated under reduced pressure and a solid residual mass was obtained. The above obtained residual sample was subjected to repeated preparative thin layer chromatography using different solvent systems, e.g solvent system 1. Methanol (5%): benzene (95%) and solvent system 2. Chloroform (60%): benzene (30%): acetic acid (10%). Three homogeneous spots were collected in solvent system 2, having Rf values of 0.87, 0.79 and 0.75 respectively. The sample with Rf value 0.79 was taken up for further study. This sample was positive in Liebermann's Burchard test[3] and gave purple colour indicating terpenoid nature of the compound and had melting point of 78^0C. This terpenoid sample positive towards to 2, 4-Dinitrophenylhydrazine test, indicating presence of aldehyde/ keto group. [4] The sample was then further analysed through various spectroscopic techniques like UV spectroscopy (UV- 1601PC, UV-Visible Spectrophotometer, Shimadzu), FT-IR spectroscopy (Perkin Elmer Spectrum- 1 Spectrophotometer), High Resolution Mass spectroscopy (JEOL- JMS 600 Instrument) and Nuclear Magnetic Resonance spectroscopy, ^{1}H & ^{13}C (Bruker Avance- 400 Spectrometer) for its proper physicochemical characterization.

Test for Presence of Keto or Aldehydic Group

1 mg of sample was dissolved in 0.4% alcoholic solution of 2, 4-Dinitrophenylhydrazine with addition of 2N HCL by capillary to maintain the acidic environment.

Results

Chemical Characterization of the Isolated Sample

The compound was reddish yellow in colour and was soluble in spectral grade methanol (Brand- Spectrochem). The melting point of the sample was 780C and it turned purple in Liebermann's Burchard test.[3]

Detection for Presence of Keto or Aldehydic Group

Addition of 2, 4-Dinitrophenylhydrazine acidic (2N HCL) solution in 1 mg of 0.4% alcoholic solution of sample yields orange yellow colour. It shows presence of an either keto or aldehydic group in the sample. [3]

UV Spectroscopy of the Isolated Sample

The methanolic spectrum of the sample showed λ max at 879.50 nm, 873.0 nm, 804.0 nm, 536.0 nm, 360.0 nm, 333.50 nm, 312.0 nm, 238.50 nm, 200.50 nm and absorbance at = 0.0014, 0.0010, 0.0005, 0.0007, 0.0001, 0.0004, 0.0033, 0.6561, 0.2520 respectively (Spectrum 1).

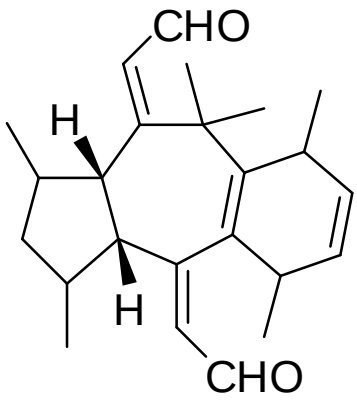
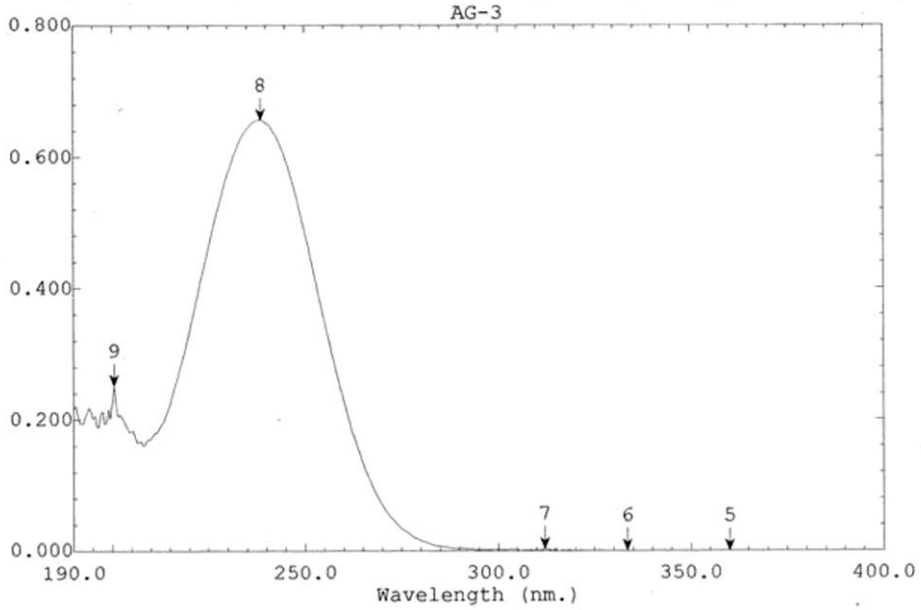


Figure 1: Structure of (2Z,2'Z)-2,2'-(3aR,10aS)-1,3,5,8,9,9-hexamethyl-1,2,3,3a-tetrahydrobenzo [f] azulene-4,10(5H,8H,9H,10aH)-diylidene) diacetaldehyde

Spectrum 1

UV spectroscopy of (2Z,2'Z)-2,2'- (3aR,10aS)- 1,3,5,8,9,9- hexamethyl-1,2,3,3a-tetrahydrobenzo [f] azulene- 4,10 (5H,8H,9H,10aH)- diylidene) diacetaldehyde



Peak Pick

No.	Wavelength (nm.)	Abs.
1	879.50	0.0014
2	873.00	0.0010
3	804.00	0.0005
4	536.00	-0.0007
5	360.00	0.0001
6	333.50	0.0004
7	312.00	0.0033
8	238.50	0.6561
9	200.50	0.2520

File Name: AG-3

Created: 14:08 07/26/12
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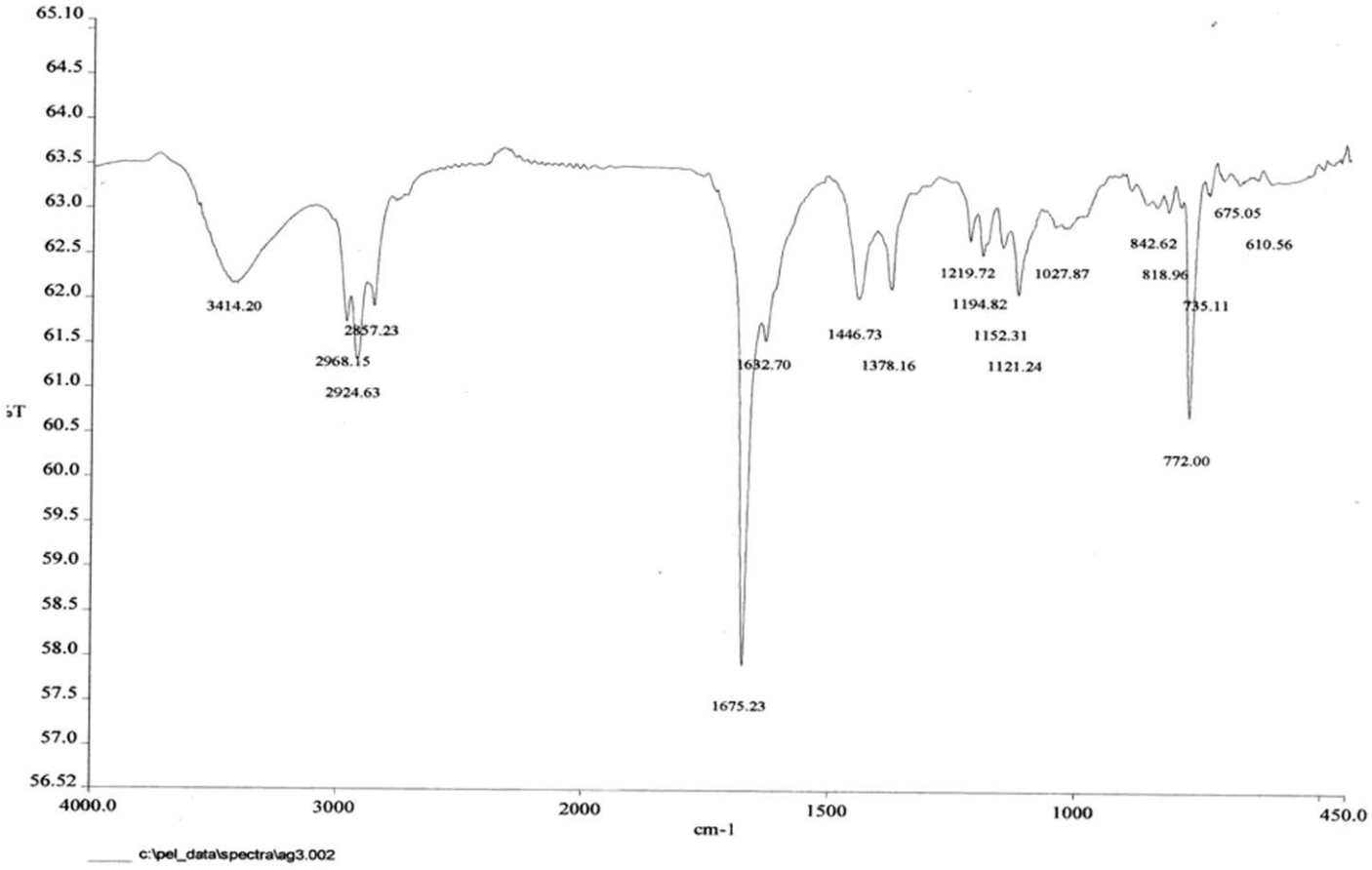
Measuring Mode: Abs.
Scan Speed: Fast
Slit Width: 1.0
Sampling Interval: 0.5

IR (FT-IR) Spectroscopy of the Isolated Sample

The IR spectrum of the sample showed n- (cm^{-1}): 2968, 2924, 2857, 1675, 1633, 1447, 1378, 1220, 1195, 1152, 1121, 843 (Spectrum 2).

Spectrum 2

IR (FT-IR) spectrum of (2Z,2'Z)-2,2'- (3aR,10aS)-1,3,5,8,9,9- hexamethyl- 1,2,3,3a-tetrahydrobenzo [f] azulene- 4,10(5H,8H,9H,10aH)-diylidene) diacetaldehyde

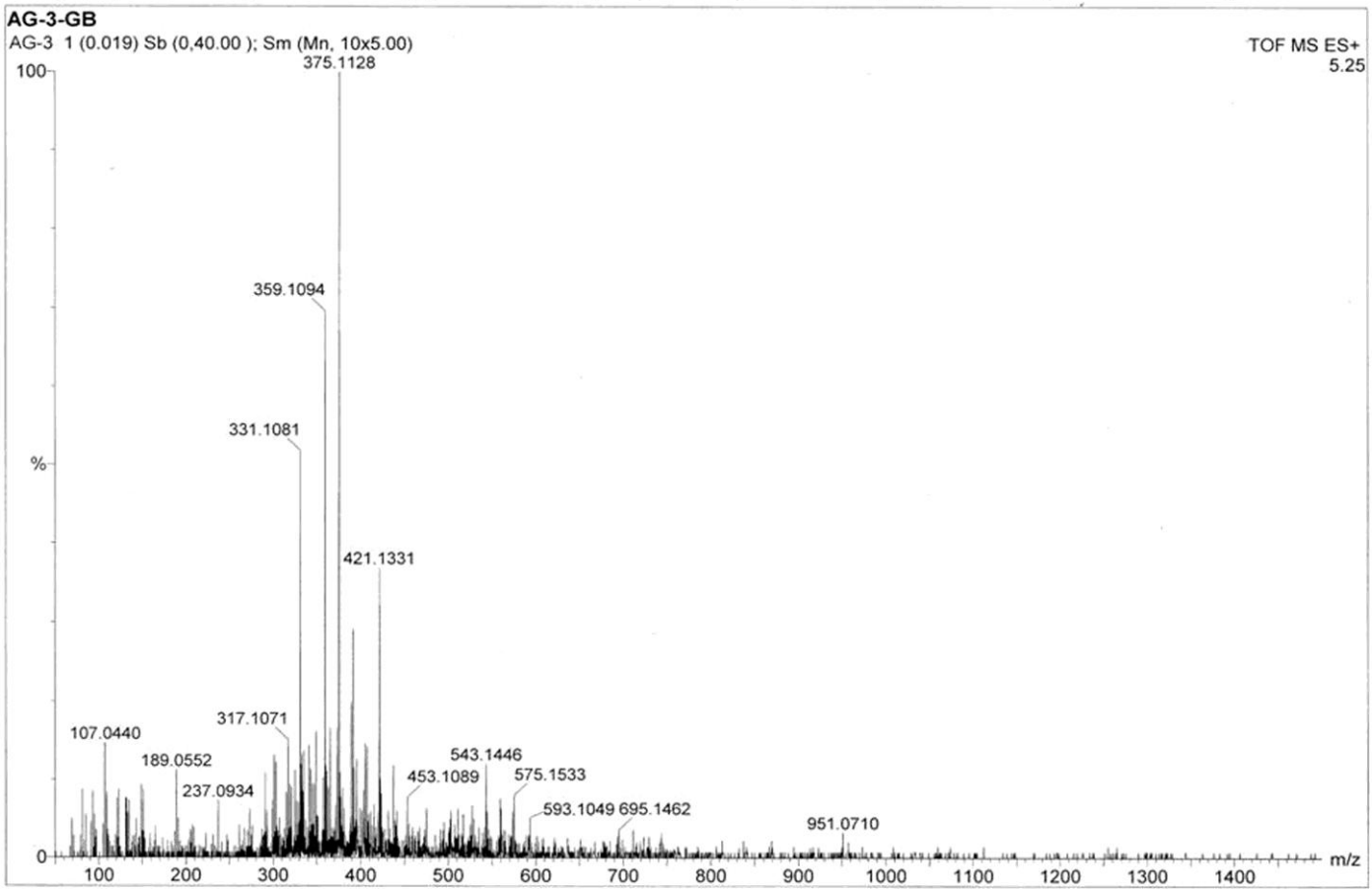


High Resolution Mass Spectroscopy of the Isolated Sample

The mass of the sample was noted as to be (TOF MS ES^+) 375.1128 (M + Na) (Spectrum 3).

Spectrum 3

High Resolution Mass spectrum of (2Z,2'Z)-2,2'- (3aR,10aS)-1,3,5,8,9,9- hexamethyl-1,2,3,3a-tetrahydrobenzo [f] azulene- 4,10(5H,8H,9H,10aH)-diylidene) diacetaldehyde



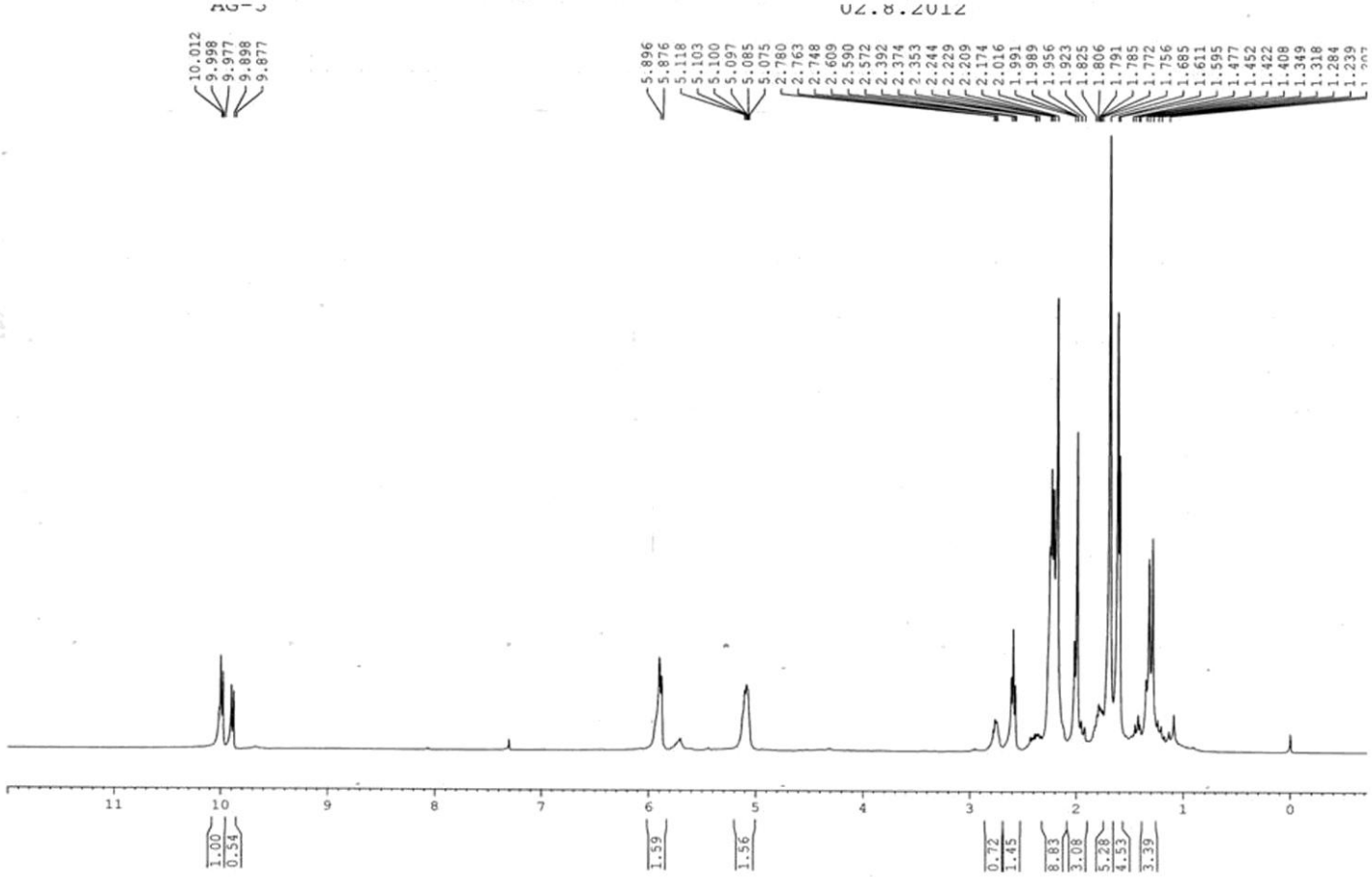
Nuclear Magnetic Resonance Spectroscopy of the Isolated Sample

^{1}H NMR (400 MHz, CDCl3):

δ. 9.99 (1H, d, J = 8.4 Hz, C=CH-CHO), 9.88 (1H, Cl, J = 8.4 Hz, C=CH-CHO), 5.88 (2H, J = 8.4 Hz, C=CH-CHO), 5.12- 5.10 (2H, m, CH=CH), 2.78-2.75 (1H, m), 2.60 (2H, t, J = 7.6 Hz, HC(Me)-CH-CH-(Me)CH), 2.24-2.17 (9H, m), 2.0 (3H, d, J= 10.0 Hz), 1.68 (6H, s), 1.60 (3H, d, J= 6.4 Hz), 1.35-1.28 (2 H, m) (Spectrum 4).

Spectrum 4

Proton NMR spectrum of (2Z,2'Z)-2,2'- (3aR,10aS)-1,3,5,8,9,9- hexamethyl- 1,2,3,3a-tetrahydrobenzo [f] azulene- 4,10(5H,8H,9H,10aH)-diylidene) diacetaldehyde

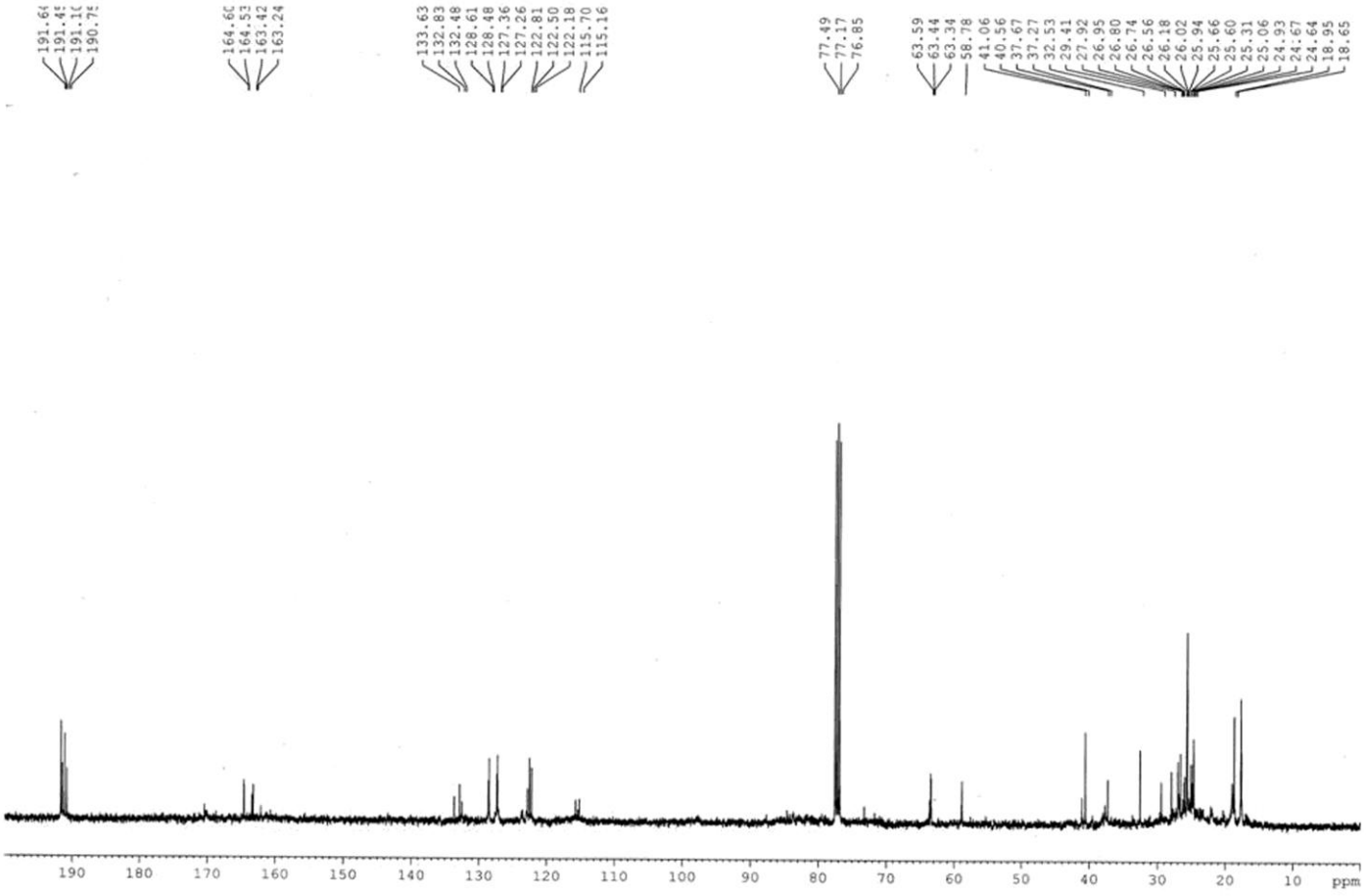


^{13}C NMR (100 MHz, $CDCl_3$):

δ. 191.64 (CHO), 191.10 (CHO), 164.6, 163.4, 133.6, 132.8, 128.5, 127.3, 122.8, 122.2, 63.4, 58.8, 40.6, 37.3, 32.5, 29.4, 28.0, 26.8, 26.6, 26.0, 25.1, 24.7, 18.6, 17.6 (Spectrum 5).

Spectrum 5

Carbon NMR spectrum of (2Z,2'Z)-2,2'- (3aR,10aS)-1,3,5,8,9,9- hexamethyl- 1,2,3,3a-tetrahydrobenzo [f] azulene- 4,10(5H,8H,9H,10aH)-diylidene) diacetaldehyde



Discussions

Interpretation of the Structure of the Isolated Compound

UV spectrum shows the presence of absorption peak (λ max) at 238.50 nm, which indicates the skeleton, should contain conjugated enone system(s). The reduced carbonyl stretching frequency (cm^{-1}) from its actual 4 value also supports presence of conjugated carbonyl group(s). 1H NMR spectrum shows the presence of 32 protons. Among which δ = 9.99 ppm (1H, d, J = 8.4 Hz) and 9.98 ppm (^{1}H, d, J = 8.4 Hz) confirms the presence of two aldehydic protons. Two of the four olefinic protons directly attached to aldehyde functionality had been obtained at δ = 5.88 ppm (2 H, d, J = 8.4 Hz). Remaining 26 protons was observed in the aliphatic region of the 1H NMR spectrum. The 24 peaks in ^{13}C NMR spectrum clearly indicate the presence of 24 different carbon atoms in which δ = 191.64 ppm and 191.10 ppm indicates the presence of two aldehydic carbons. The HRMS spectrum of the isolated compound was found 375.1121 (M + Na). Hence, the molecular formula of the isolated fraction must be $C_{24}H_{32}O_2$ and its structure was shown in Figure 1.

Acknowledgements

This work was supported by Grants in Aid from the DST-PURSE (Grant No. FD/1626, dated: 29.1.2013) and University of Kalyani (Grant No. Rev/ 1124 of 12-13, dated: 28.2.2013), Nadia, West Bengal.

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