NOVATEUR PUBLICATIONS
INTERNATIONAL JOURNAL OF INNOVATIONS IN ENGINEERING RESEARCH AND TECHNOLOGY [IJIERT]
ISSN: 2394-3696 Website: ijiert.org
VOLUME 7, ISSUE 8, Aug.-2020

STUDY OF STRUCTURE NEW ORGANIC COMPOUND WITH NMR SPECTROSCOPY

KHOLMIRZAEVA KHILOLA
Department of Analytical Chemistry, Samarkand State University, Uzbekistan
E-mail id: (hilola.xolmirzaeva@mail.ru)

KHOLMIRZAEV SHAVKAT
Chemistry Teacher
Samarkand, Uzbekistan

ABSTRACT

Investigation of the structure of substances isolated chemically or by synthesis first of all begins with the determination of it is structure. The new compound structure were established on the basis of HR-MS and NMR as well as by comparison with the literature data. Theoretical aspects of one dimensional ^{1}H NMR, ^{13}C NMR, two dimensional NMR methods as DEPT, HSQC, HMBC and NOESY has been learnt and used to study determine the structure and changes, Peer review of research in this area is important and has more practical value.

KEYWORDS: lignanamides, methanol-d$_4$, antioxidant, acetyl cholinesterase inhibitor, spin-spin effect.

INTRODUCTION

Investigation of the structure of substances isolated chemically or by synthesis first of all begins with the determination of its structure. After determining the structure, their physical and chemical properties are studied. When solving the problem encountered in the process of such studies, research methods develop and experimental materials for the development of the theory of the structure of matter accumulate. Therefore, the determination of the structure of the molecule of compound is relevant. The purpose of this study is to determine the structure of the molecule of the isolated substance. To accomplish this task, one-dimensional proton and ^{13}C NMR spectra, DEPT, COSY, HSQC, HMBC and NOESY spectra were recorded and interpreted. Main results of work: the spatial structure of the isolated substance is reliably determined.

MATERIALS AND METHODS

The new compound was isolated as a colorless amorphous powder. The molecular formula of it was determined to be $C_{34}H_{31}N_2O_8$ by positive-ion HR-ESI-MS, suggesting 20 degrees of unsaturation. Samples of hydrogen atoms were dissolved in methanol-d$_4$ (CD_3OD) replaced by deuterium. In the spectra of the ^{13}C and ^{1}H solutions, methanol shows intense signals belonging to the carbon nuclei of the CD_3 group and the nuclei of the residual hydrogen atoms of this groip's protons. The chemical shifts of these signals were 49.0 and 4.84 respectively. Chemical shifts of the signals in the NMR spectra of the test sample were calculated relative to the signals of the solvent. The signal of these two lines was measured relative to the TMS signals, 4.84(^{1}H) and 49.0 (^{13}C) [1]. All spectra were recorded at room temperature. 2D experiments COZY (Correlation Sectroscopy), HETCOR (Hetro-correlation spectroscopy or Hetero-COZY) were carried out in the sequential mode of standard pulses of NMR spectrometer.

When recording the proton (At) spectra, the recording time was 4 second, the spectral propagation with was 5 kHz, and the number of signal sets that is interferograms was 32. In the carbon-13C and DEPT (At) experiments, it was 4 second, the spectral propagation was 24 k Hz, and the number of collectors was 25000 and 8000 respectively. The Nuclear Overhauser Effect (NOE) experiment was performed on a 2D spectrometer mode.

Due to the large molecular weight of the substance we studied, it can be ionized only by MALDI or electrospray methods. Because when ionized by other methods, it can decompose. Therefore, the mass spectrum was ionized using electrospray ionization (ESI).

As the aim of the study, a organic compound selected by the chemical methods of the aerial part of the plant was selected by scientific employees of the Institute of Plant Substances Chemistry of the Academy of Sciences of Uzbekistan.

ANALYSIS AND RESULTS

Using date on the integrated spectrum intensity, we calculate the number of protons in the molecule. Calculations show that there are 29 protons in molecule. In the aromatic field remain 6-7 protons, so there should be two more benzene rings. A single signal is divided into a doublet of a doublet (J_1=3856.75, J_2=3854.58, J_3=3848.67 and J_4=3846.53 Hz, J=2.17 Hz), which indicates the presence of one proton at 3 and 4 communication distances from this proton. The frequencies of the equations are J_1=3908.83 and J_2= 3906.70 Hz (J=2.13 Hz). The closest are the slightly enlarged and well-separated doublet (J_1=4127.65 and J_2=4125.59 Hz, J=2.06 Hz) and the doublet of the doublet (J_1=4127.67 and J_2=4096.13 and J_3=4094.08 Hz, one not visible, J=2.05 Hz) [2, 3].

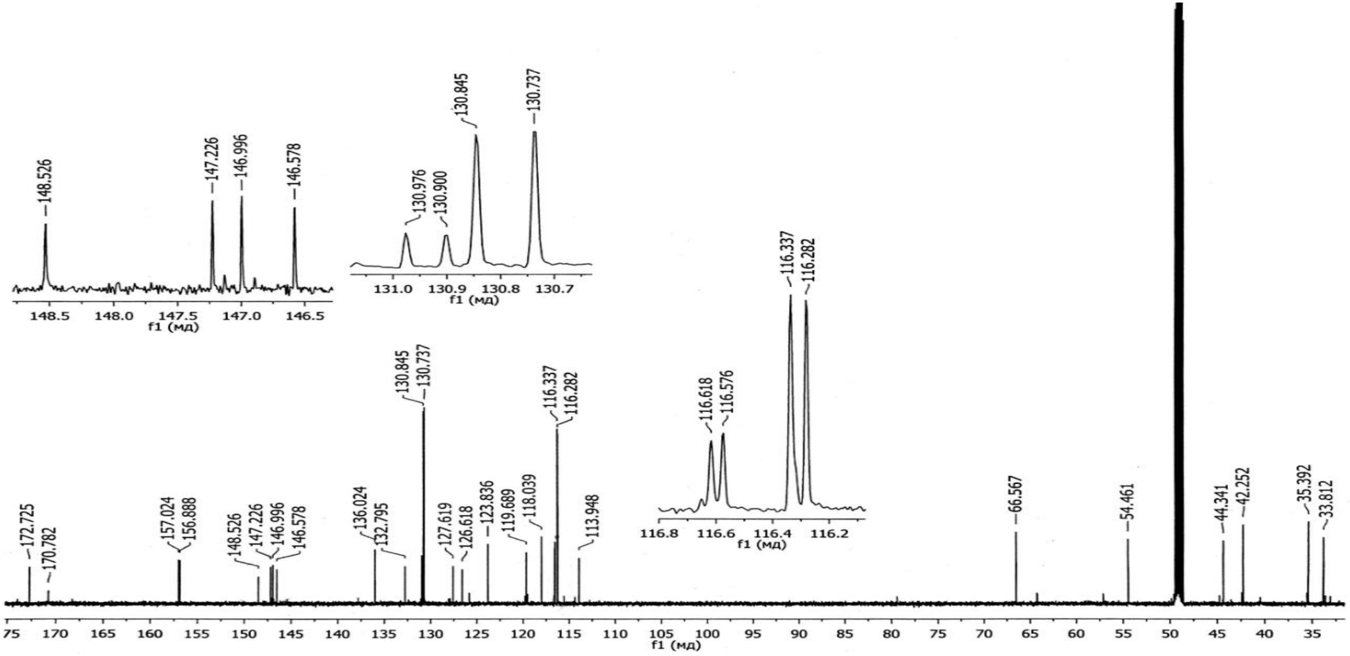

Figure 1. ^{13}C NMR spectrum in which the spin-spin interaction between the carbon nuclei and the hydrogen atoms of the substance under study is completely excluded

Here, the intensity is inversely proportional to the spin-lattice relaxation time of the corresponding nucleus. The signals of nuclei forming bonds with oxygen atoms with high electronegativity are visible in the lower field (Figure 1). The total number of carbon signals in the spectrum is 30. The molecular formula of the substance's molecule, found by mass spectrometry, contains 34 carbon atoms. If the molecular formula is correct, 4 signals will belong to equivalent carbon atoms. Chemical shifts in the spectrum are 172.73, 170.78 signals to carbon atoms bound by oxygen via a double bond, 157.02 and 156.88 belong to the carbon atoms of the aromatic ring bonded to one oxygen atom [1].

The coordinates some of the cross signals observed in the COZY spectrum under consideration (chemical shifts or groups of protons under the influence of multual spin –spin) were determined by drawing horizontal and vertical straight lines. The COZY spectrum contains cross-signals related to the following groups: $-CH_2-CH_2-$ group in the structural formula, vicinal spin-spin effect (numbers 7```-8```), = >CH–CH< group vicinal (7``-8``),$-CH_2-$ (8, δ=2.88 and 8, δ=3.81) geminal spin-spin effect, $-CH_2-$ (8```, δ=3.16 and 7, δ=2.74) germinal spin-spin effect.

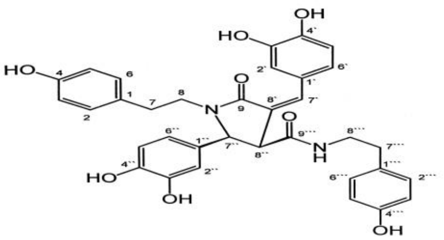

Figure 2. Structures of compound.

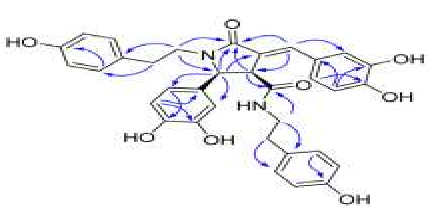

Figure 3. Key HMBC correlations for compound.

The ^{1}H and ^{13}C NMR spectra of compound indicated that it was also a lignanamide compound with two tyramine moieties [δ 6.99 (2H, d, H-2``,6``), 6.71 (2H, d, H-3``,5``), 2.55, 2.77 (2H, m, H-7``), 2.92, 3.84 (2H, m, H-8``); δ 6.95 (2H, d, H-2```,6```), 6.71 (2H, d, H-3```,5```), 2.62, 2.77 (2H, m, H-7```), 3.19, 3.45 (2H, m, H-8```)] and two ABX-type coupled aromatic moieties [δ 6.91 (1H, d, J = 2.0 Hz, H-2), 6.79 (1H, d, J = 8.2 Hz, H-5), 6.87 (1H, dd, J = 2.0, 8.2 Hz, H-6); and δ 6.54 (1H J = 2.1 Hz, H-2`), 6.77 (1H, d, J = 8.1 Hz, H-5`), 6.45 (1H dd, J = 2.1, 8.1 Hz, H-6`)] (Table 1). In the HMBC spectrum, the correlation signals of H-8`` with C-9 (δ 169.3) and H-8``` with C-9` (δ 171.3) indicated that the two tyramine groups were linked to C-9 and C-9`, respectively. The correlation signals between H-8`` (δ 2.92 and 3.84) and C-9 (δ 169.3), C-7` (δ 65.1), the correlations between H-7` (δ 4.27) and C-9′ (δ 171.3), C-8 (δ 125.1), C-9 (δ 169.3), and the correlations between H-7 (δ 7.42) and C-9 (δ 169.3), C-8` (δ 53.0) led to a γ-lactam central moiety as shown in the structure of compound (Figure 3). The small J $_{7',8'}$ value (2.4 Hz) of compound indicated that the two protons were cis-oriented. The structure of it was similar to that of heliotropamide, 38 except for the disappearance of the methyl groups. Thus, the structure of compound was determined as (2,3-cis)-4-(3,4-dihydroxybenzylidene)-2-(3,4-dihydroxy phenyl)-N,1-bis(4-hydroxyphenethyl)-5-oxopyrrolidine-3-carboxamide and was named 3,3′-demethyl-heliotropamide (Figure 2).

Table 1. ^{1}H and ^{13}C NMR Data for new Compound in CD_3OD

C atom	δ_C	δ_H (J/Gs)	COSY(H)	HMBC (C)
1	130.90			
2	130.85	6.96, d, (8.3)	3, 6	7, 6
3	116.34	6.69, d, (8.3)	2, 5	5, 1, 4
4	157.02			
5	116.34	6.69, d, (8.3)	6, 3	3, 1, 4
6	130.85	6.96, d, (8.3)	5, 2	7, 2
7	33.81	2.59, m 2.74, dt, (14.3, 7.8)	8, 7	2, 6, 8 2, 6, 8
8	44.34	2.89, dt, (14.3, 7.5) 3.81, m	7, 8, 8``	1, 9, 7``, 7 1, 9, 7``, 7
9	170.78			
1`	127.62			
2`	118.04	6.88, d, (2.0)	5`, 6`	6`, 7`, 4`, 3`
3`	146.58			
4`	148.53			
5`	116.62	6.76, d, (8.2)	6`, 2`	1`, 3`, 4`
6`	123.84	6.83, dd, (8.2, 2.0)	5`, 2`	2`, 7`, 4`
7`	136.02	7.38, d, (2.2)	8``	8``, 2`, 6`, 8`, 9, 9```
8`	126.62			
1``	132.80			
2``	113.95	6.52, d, (2.1)		7``, 6``, 4``
3``	147.23			
4``	147.00			
5``	116.58	6.74, d, (8.0)	6``	1``,3``
6``	119.69	6.42, dd, (8.0, 2.1)	5``	7``, 2``, 4``
7``	66.57	4.25, d, (2.5)	8``, 8	9,9```,2``,6``,1``,8``
8``	54.46	3.81, dd, (2.5, 2.2)	7`, 7``	9```, 8`, 1``,7`
1```	130.98			
2```	130.74	6.92, d, (8.3)	6```, 3```	7```, 6```, 4```
3```	116.28	6.67, d, (8.3)	2```	5```, 1```, 4```
4```	156.89			
5```	116.28	6.67, d, (8.3)	3```, 6```	3```,1```,4```
6```	130.74	6.92, d, (8.3)	2```, 5```	7```,2```,4```
7```	35.39	2.52, m 2.57, m	8```	2```,6```,8``` 2```,6```,8```
8```	42.25	3.16, dt, (13.5,7,5) 3.42, dt, (13.5,7.8)	7```, 8```	1```, 9```,7``` 1```, 9```,7```
9```	172.73			

^{a}δ in ppm, frequency was 600 MHz for 1H NMR and 150 MHz for 13C NMR, assignments of 1H, 13C NMR data were based on COSY and HMBC experiments.

CONCLUSIONS AND RECOMMENDATIONS

To determine the structure of the molecule of the separated substance, the most modern and effective methods that are available today are used. As a result, the structure of the molecule was comprehensively studied. As a result of these studies, the structure of the molecule of the compound was finally established.

Theoretical aspects of one dimensional ^{1}H NMR, ^{13}C NMR, two dimensional NMR methods as DEPT, HSQC, HMBC and NOESY has been learnt and used to study determine the structure and changes, Peer review of research in this area is important and has more practical value.

REFERENCES

1) Prech E., Blumann F. Affolter K., The definition of the structure of organic compounds (table of spectral date), Moscow, “the world”, 2006, 438 p.103, 89 p.
2) Mistry B.D., A Handbook of Spectroscopic Data Chemistry, (UV, IR, PMR, ^{13}C NMR and Mass Spectroscopy), Oxford book company, 2009, 242 p.
3) Website with a collection of NMR (^{1}H, ^{13}C), IR, raman and mass spectra of chemicals: AIST:RIO-DB Spectral Database for Organic Compounds,SDBS
4) Yuefang Zhou, Shanshan Wang, Hongxiang Lou, Peihong Fan. “Chemical constituents of hemp (Cannabis sativa L.) seed with potential antineuroinflammatory activity”. Phytochemistry Letters, Vol 23. 57-61, 2018.
5) Bing-You Yang, Xin Yin, Yan Liu, Hong-Liang Ye, Mei-Ling Zhang, Wei Guan, Hai-Xue Kuang ”Bioassay-guided isolation of lignanamides with potential anti-inflammatory effect from the roots of Solanum melongena L”. Phytochemistry Letters, Vol 30. 160-164, 2019.
6) Hui Chen, Yu-Jie Lic, Yan-Jun Suna, Jian-Hong Gonga, Kun Dua, Yan-Li Zhang, Cheng-Fu Sub, Qian-Qian Hanc, Xiao-Ke Zheng, Wei-Sheng Feng. “Lignanamides with potent antihyperlipidemic activities from the root bark of Lycium chinense”. Fitoterapia, Vol 122. 119-125, 2017.
7) Xue-Yan Huang, Zhao-Xiang Shao, Li-Jun An, Jing-Jing Xue, Da-Hong Li, Zhan-Lin Li, Hui-Ming Hua. “New lignanamides and alkaloids from Chelidonium majus and their anti-inflammation activity”. Fitoterapia, Vol 139. 104359, 2019.
8) Wenjie Huang, Chuan Li, Yihai Wang, Xiaomin Yi, Xiangjiu He. “Anti-inflammatory lignanamides and monoindoles from Alocasia macrorrhiza”. Fitoterapia, Vol 117. 126-132, 2017.
9) Chen-Xi Lia, Xiao-Yu Songa, Wen-Yu Zhaoa, Guo-Dong Yaoa, Bin Linb, Xiao-Xiao Huanga, Ling-Zhi Lia, Shao-Jiang Song. “Characterization of enantiomeric lignanamides from Solanum nigrum L. and their neuroprotective effects against MPP+-induced SH-SY5Y cells injury”. Phytochemistry,Vol 161. 163 171, 2019.
10) Wang Pei-Pei, Zhao Guo-Wei, Xia Wen, Han En-Ji, Xiang Lan. ”A new flavonol C-glycoside and a rare bioactive lignanamide from Piper wallichii Miq. Hand.-Mazz”. Chinese Journal of Natural Medicines, Vol 12, No. 5, pp. 0377−0381, 2014.