RESOURCE UTILIZATION OF *SAMBUCUS WILLIAMSII* HANCE ROOT

by

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Original scientific paper
https://doi.org/10.2298/TSCI190605041C

In recent years, more and more attention has been paid to bio-energy. People are eager to find new substances from sustainable forest products for energy research. As an important forest resource, Sambucus williamsii Hance has gradually attracted people's attention. Therefore, in order to explore a new way of comprehensive utilization of Sambucus williamsii Hance, the root samples of Sambucus williamsii Hance were collected and extracted with ethanol, benzene/ethanol and methanol, respectively. Fourier transform infrared spectroscopy (FT-IR), thermogravimetry (TGA) and pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) were used to detect the treated samples, and various substances in Sambucus williamsii Hance root were studied in depth. The results show that the thermal decomposition products of raw material powders and extracts contain many chemical substances. Such as (1R) - (-) –Myrtenal, D-Mannose, Furfural, O-Xylene, Phenol, 2,6-dimethyl-. These substances have broad application prospects in chemical industry, bio-medicine, food additives and other fields, thus providing a theoretical basis for the rational use of Sambucus williamsii Hance.

Key words: *Sambucus williamsii Hance root, FT-IR, TGA, Py-GC-MS*

Introduction

As the basic material for human survival, energy is driving force for human development, and its supply stability is an important guarantee for the long-term stability of the country [1, 2]. As a kind of renewable energy, bio-energy is the form of solar energy stored in biomass in other forms [3]. It comes from the photosynthesis of green plants directly or indirectly, and then converts into fuels in different states. It is one of the most promising fossil substitutes [4, 5]. Therefore, in order to explore new bio-energy sources, the potential of *Sambucus williamsii* Hance in this area was studied.

Sambucus williamsii Hance belongs to deciduous shrubs or small trees. It is also known as Daogaolao, Cutting, Big Jiegudan and so on. It has strong adaptability, and is widely distributed in China [6, 7]. It is commonly found in slopes, shrubs, ditches, roadsides, houses and other places at 540-1600 m above sea level [8]. *Sambucus williamsii* Hance has various functions, but its medicinal value is remarkable. Its stem and branch can be used to dispel wind

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and dampness, promote blood circulation and relieve pain, root or root bark can cure diarrhea, edema, injury and scald, and leaf can promote blood circulation and relieve blood stasis and pain [9, 10].

Although *Sambucus williamsii* Hance is a famous tree species in China, there are few studies on it at present, which results in its ineffective use. In view of this situation, *Sambucus williamsii* Hance root was sampled and treated in this experiment. Then the functional groups of *Sambucus williamsii* Hance root powder during heating were studied by FT-IR spectroscopy, differential scanning calorimetry (TG), Py-GC-MS. Pyrolysis reaction analysis of the change rule and function under different treatment conditions, then provide a theoretical basis for the follow-up development and utilization of bio-energy.

Material and methods

Experimental materials

Samples of *Sambucus williamsii* Hance root were collected from Luanchuan County, Henan Province. The root samples were crushed by a crusher. Some of the samples were sifted by 40-60 meshes and then dried at 55 °C and 0.01 MPa in vacuum. The remaining *Sambucus williamsii* Hance root samples were extracted with ethanol, benzene/ethanol (volume ratio 1:1) and methanol reagent respectively [11].

Extraction by different solvents

Samples from root were weighed at 10 g (accuracy: 0.1 mg) and put into distillation bottles. The 300 ml ethanol, benzene/ethanol and methanol were added respectively. Mixed solvents were extracted by Full Automatic Soxhlet Extractor (FOSS) [12]. Extraction conditions: After 12 hours of room temperature immersion, the mixture of different reagents was extracted for 5 hours at 79 °C, 67 °C and 65 °C, respectively, and then filtered with filter paper soaked with different reagents to obtain different extracts. The filtrate was evaporated and concentrated to about 20 ml at 45 °C and 0.01 MPa in vacuum [13].

The FT-IR analysis

The FT-IR spectra of the extracted samples were obtained by FT-IR spectrophotometer (Thermo Fisher Scientific IS10) using KBR disc containing 1.00% fine grinding samples. The instrument records infrared molecular absorption, infrared spectrum acquisition, spectral smoothing and baseline correction. Infrared spectroscopy usually takes wave (σ) as abscissa to indicate the position of absorption peak, and vertical axis transmittance (t%) to indicate absorption intensity [14, 15].

The TG analysis

The original powder samples from *Sambucus williamsii* Hance root were analyzed by thermogravimetric analyzer (SDT Q600 V20.9 Build 20). The equilibrium gas is nitrogen, and its release rate is 100 ml/min. The temperature program of TG starts at 30 °C and rises to 900 °C at the rate of 5 °C/min, 25 °C/min and 50 °C/min, respectively, and keeps constant temperature at 900 °C for 5 minutes [16].

The Py-GC-MS analysis

The Py-GC-MS (Agilent 7890B-5977B) was used to analyze the powders of *Sambucus williamsii* Hance root. With high purity helium as carrier gas, pyrolysis temperature 850 °C, pyrolysis time 30 seconds, pyrolysis product conveyor line and sampling valve temperature

300 °C, TR-5 ms column, capillary column (30 m × 250 μm × 0.25 μm), shunt mode, shunt ratio 50:1, shunt rate 50 ml/min, GC-PR temperature starts at 40 °C for 2 minutes, and rises to 120 °C at a rate of 5 °C/min, then increases to 200 °C at a rate of 10 °C/min Continue for 2 minutes. The temperature of ion source (EI) is 230 °C and the scanning range is 30-600 amu [17, 18].

Results and analysis

Infrared spectroscopic analysis

According to the relationship between organic compounds and functional groups, the infrared spectra of different extracts from *Sambucus williamsii* Hance roots were observed and compared, fig. 1. The result showed that the absorption peaks near 3430-3280 cm^{-1} may be caused by contractive vibration of -OH in liquid water or alcohols and phenols, the absorption peaks at 2950-2840 cm^{-1} may be caused by contractive vibration of C-H in CH_3 and CH_2, and the absorption peaks at 1670-1570 cm^{-1} may be caused by contractive vibration of conjugated and non-conjugated C=O, C=C and amide bonds. The peak at 1500 cm^{-1} may be caused by the vibration of C-C bond in benzene ring. The absorption peak at 1450-1350 cm^{-1} may be caused by O-H bending vibration in carboxylic acid. The absorption peaks at 1100-1020 cm^{-1} may be caused due to the stretching vibration of C-O in aryl alkyl ethers and vinyl ethers [19, 20]. As can be seen from the figure, the absorption peaks of *Sambucus williamsii* Hance root extracts are mainly concentrated in the range of 3430-3280 cm^{-1}, 2950-2840 cm^{-1} and 1670-1100 cm^{-1}. According to the relevant information, the extracts of the three reagents may contain hydrocarbons (saturated and unsaturated), alcohols, phenols, aldehydes, ketones, ethers and aromatic compounds.

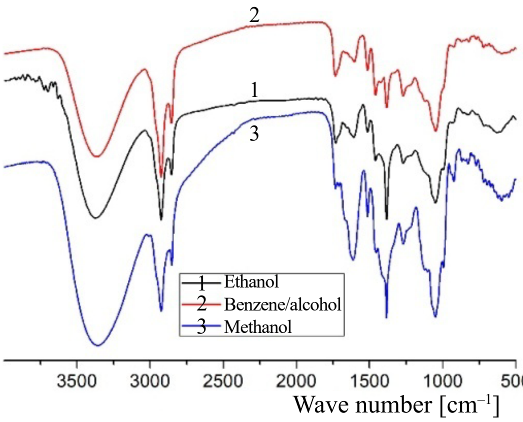

Figure 1. Infrared spectra of different extracts from *Sambucus williamsii* Hance root

Analysis of pyrolysis characteristics of Sambucus williamsii Hance root

The TGA reflects the thermal stability of the material, which lays a foundation for further study of its flame retardancy. The TGA was used to determine the mass change of the samples at 5 °C, 25 °C and 50 °C/min heating rates. The curves of TGA and DTG were obtained, fig. 2.

The pyrolysis process of *Sambucus williamsii* Hance root can be divided into three stages. In the first stage (50-260 °C), the mass loss accounts for about 7% of the total weight loss in the pyrolysis process, which is mainly caused by free water and some volatile small molecular substances in the sample. In the second stage (270-450 °C), the main stage of sample pyrolysis is

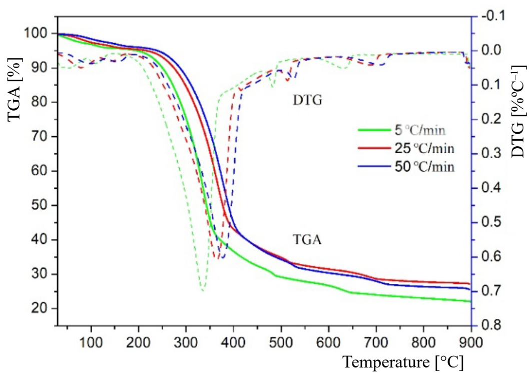

Figure 2. The TGA and DTG curves of three rates of *Sambucus williamsii* Hance root

the pyrolysis stage. The pyrolysis reaction is more intense. In the pyrolysis process, the mass loss is mainly caused by some volatile small molecular substances. It accounted for 56% of the total weight loss. At the same time, with the increase of heating rate, the temperature at the beginning, peak and end of thermal decomposition process changes slightly to high temperature. At this stage, DTG curve shows a significant peak, and the maximum temperature of weight loss rate increases with the increase of heating rate. The third stage (480-900 °C) is the final pyrolysis process of *Sambucus williamsii* Hance root, which mainly occurs carbonization reaction. With the reaction proceeding, the TGA curve gradually tends to straight line, and the weight loss rate of thermal decomposition process remains basically unchanged after 700 °C [21, 22]. The thermal decomposition process of *Sambucus williamsii* Hance root at 900 °C was described by TGA experiment, which provided a reference for the future study of the thermal decomposition of *Sambucus williamsii* Hance.

Analysis of pyrolysis productsof Sambucus williamsii Hance root

Under the experimental conditions, the pyrolysis gas of *Sambucus williamsii* Hance root was determined. The gas chromatography and mass spectrometry data were obtained by GC-MS, and the related mass spectrometry data were analyzed and consulted.

A total of 143 chromatographic peaks were detected by Py-GC-MS analysis, a total of 106 compounds were identified, fig. 3. Some of them were as follows: Acetic acid (10.007%), 1H-Indene, 3-methyl-(1.241%), Phenol (2.261%), Bicyclo[4.2.0]octa-1,3,5-triene (2.559%), 3-Chloro-4-hydroxyiminocarane (1.162%), Phenol, 3-ethyl-(2.245%), Phenol, 3-methyl-(4.978%), 1,3,5-Cycloheptatriene (4.256%), 1,3-Hexadien-5-yne (4.498%), 2-Isopropoxyphenol (2.181%), 3-Vinyl-1-cyclobutene (1.931%), 4-Penten-1-ol (4.924%), Cyclopropyl carbinol (8.125%), trans-Hexa-2,4-dienyl acetate (1.932%) and so on. Some of them have important functions. (1R) - (-) - Myrtenal is a kind of perfume, which has a wide range of uses and is an important fine chemical intermediate. It can further synthesize a series of more valuable perfumes, such as Perilla sauce [23]. The D-Mannose is used in cell culture and molecular biology as well as in biochemical reagents and sweeteners. Furfural is mainly used as industrial solvent to produce furfuryl alcohol, furoic acid, tetrahydrofuran, gamma-pentyl lactone, pyrrole, tetrahydropyrrole, *etc*. It is used as raw material of organic synthesis, synthetic resin, varnish, pesticide, medicine, rubber and paint, etc. Some derivatives of furfural have strong bactericidal activity and broad antimicrobial spectrum [24, 25]. Furfural as a solvent can selectively extract unsaturated components from petroleum and vegetable oils, and at the same time extract aromatic components from lubricants and diesel oil with furfural to improve the quality

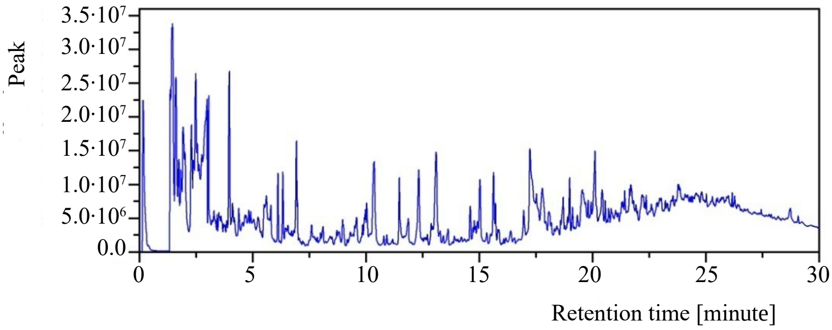

Figure 3. Total ion atlas of thermal pyrolysis of *Sambucus williamsii* Hance root

of these products [26]. The O-Xylene can be used to produce phthalic anhydride, dyes, pesticides and drugs, such as vitamins. It can also be used as an additive for aviation gasoline [27]. Phenol has an important applications in chemical raw materials, alkyl phenols, synthetic fibers, rubber, medicine, pesticides, spices, dyes, coatings and oil refining industries. In addition, phenol can also be used as solvent, experimental reagent and disinfectant [28, 29]. Phenol, 2,6-dimethyl- is used in the production of polyphenyl ether resins, photographic agents, pesticides, polyesters and polyether resins. It is also the raw material of antiarrhythmic drugs for slow heartbeat [30-32]. Ethylbenzene is mainly used to produce styrene, then to produce styrene homopolymer and styrene-based copolymers (ABS, AS, *etc.*); a small amount of ethylbenzene is used in organic synthesis industry, such as the production of acetophenone, ethylanthraquinone, p-nitroacetophenone, methyl phenyl methyl ketone and other intermediates. Ethylbenzene is used in medicine as an intermediate for synthesizing chloramphenicol and chloramphenicol. It is also used in perfumes and solvents [33, 34]. Phenol, 3-methyl-is mainly used as pesticide intermediates in the production of insecticides such as fenthion, methomyl and pyrethroid-like isophenoxybenzaldehyde. It is also used in analytical reagents, organic synthesis, color film, resin plasticizer, perfume, medicine, antioxidants and other industries requiring the use of m-cresol in chemical industry [35, 36]. Bicyclo [4.2.0]octa-1,3,5-triene monomers possess thermodynamic stability of aromatic compounds and dynamic reactivity of strain rings. After heating to 200 °C, the Quaternary ring opens and forms a highly active polymerizable intermediate. The polymerizable intermediate can not only react with Diels-Alder addition of diene monomers, but also react with each other to form polymers [37-39]. The functions of some other substances need to be further developed and studied.

Conclusions

The infrared absorption peaks of different extracts from *Sambucus williamsii* Hance roots were mainly between 3430-3280 cm^{-1}, 2950-2840 cm^{-1} and 1670-1100 cm^{-1}. According to the relevant information, the extracts of the three reagents may contain hydrocarbons (saturated and unsaturated), alcohols, phenols, aldehydes, ketones, ethers, aromatic compoundsand so on.

The TGA shows that the pyrolysis process of *Sambucus williamsii* Hance root original powder can be divided into three stages. The first stage (50-260 °C) is relatively slow thermal decomposition with low weight loss rate, mainly evaporation of liquid water molecules; the second stage (270-450 °C) is an important stage of thermal decomposition with weight loss about 56%; the third stage (480-900 °C) is the carbonization of some high temperature resistant materials.

High temperature pyrolysis, the original powder of *Sambucus williamsii* Hance root contained more bio-active substances, after consulting relevant information and analyzing the results of previous studies, most of these bio-active substances play an important role in bio-energy, chemical raw materials, bio-medicine and food industry, it is worthwhile for us to explore its value deeply.

In conclusion, *Sambucus williamsii* Hance root has high value. The research not only provides guidance for the development and utilization of the potential value of *Sambucus williamsii* Hance root, but also reminds us to pay attention to the research and development of its deeper utilization value while utilizing the forest resources endowed by nature, which not only points out the direction of development for the utilization of contemporary resources, but also for future generations. Classification lays a solid foundation for further exploration of energy resources.

References

[1] Atteridge, A., Savvidou, G., Development Aid for Energy in Small Island Developing States, *Energy, Sustainability and Society, 9* (2019), Mar., 10
[2] Ishihara, T., Sofronis, P., Focus on Carbon-Neutral Energy Science and Technology, *Science and Technology of Advanced Materials, 19* (2018), 1, pp. 481-485
[3] Kumar, S., Ghosh, P., Sustainable Bio-Energy Potential of Perennial Energy Grass from Reclaimed Coalmine Spoil (Marginal Sites) of India, *Renewable Energy, 123* (2018), Aug., pp. 475-485
[4] Apiraksakorn, J., *et al.*, The Evaluation of Bio-Energy Produced from Ethanol Fermentation Using Corncob Dust Hydrolysate, *Energy Procedia*, *138* (2017), Oct., pp. 145-150
[5] Gonzalez-Garcia, S., Bacenetti, J., Exploring the Production of Bio-Energy from Wood Biomass, Italian Case Study, *Science of the Total Environment*, *647* (2019), Jan., pp. 159-168
[6] Kuang, H., *et al.*, Chemical Constituents from Sambucus Williamsii Hance Fruits and Hepatoprotective Effects in Mouse Hepatocytes, *Natural Product Research, 32* (2018), 17, pp. 2008-2016
[7] Xiao, H., *et al.*, Phytochemicals and Potential Health Effects of Sambucus Williamsii Hance (Jiegumu), *Chinese Medicine, 11* (2016), July, 36
[8] Zhang, Y., *et al.*, Study of the Mechanisms by Which Sambucus Williamsii Hance Extract Exert Protective Effects Against Ovariectomy-Induced Osteoporosis in Vivo, *Osteoporosis International, 22* (2011), 2, pp. 703-709
[9] Wang, Z., *et al*., Two New Iridoid Glycosides from the Root Barks of Sambucus Williamsii Hance, *Molecules, 17* (2012), 2, pp. 1830-1836
[10] Xiao, H., *et al*., New Lignans from the Bioactive Fraction of Sambucus Williamsii Hance and Proliferation Activities on Osteoblastic-Like UMR106 Cells, *Fitoterapia, 94* (2014), Apr., pp. 29-35
[11] Jiang, S. C., *et al*., Molecules and Functions of Rosewood: Dalbergia Stevenson, *Arabian Journal of Chemistry*, *11* (2018), 6, pp. 782-792
[12] Shiung, L. S., *et al*., Microwave Pyrolysis Valorization of Used Baby Diaper, *Chemosphere, 230* (2019), Sept., pp. 294-302
[13] Peng, W., *et al*., Biomedical Molecular Characteristics of YBSJ Extractives from Illicium Verum Fruit, *Biotechnology & Biotechnological Equipment, 27* (2013), 6, pp. 4311-4316
[14] Kyomugasho, C., *et al*., FT-IR Spectroscopy, a Reliable Method for Routine Analysis of the Degree of Methylesterification of Pectin in Different Fruit- and Vegetable-Based Matrices, *Food Chemistry*, *176* (2015), June, pp. 82-90
[15] Bazin, P., *et al*., A Thermogravimetric and FT-IR Study of the Reduction by H 2 of Sulfated Pt/Ce x Zr 1− x O 2 Solids, *Applied Catalysis B, Environmental, 90* (2009), 3, pp. 368-379
[16] Jain, A. A., *et al*., Processing of TGA Data: Analysis of Isoconversional and Model Fitting Methods, *Fuel, 165* (2016), Feb., pp. 490-498
[17] Machado, M. A., *et al*., Renewable Fuel Production from Hydropyrolysis of Residual Biomass Using Molybdenum Carbide-Based Catalysts: An Analytical Py-GC/MS Investigation, *Catalysis Today, 302* (2018), Mar., pp. 161-168
[18] Ortiz-Herrero, L., *et al*., Direct and Indirect Approaches Based on Paper Analysis by Py-Gc/Ms for Estimating the Age of Documents, *Journal of Analytical and Applied Pyrolysis*, *131* (2018), May, pp. 9-16
[19] Cai, H., *et al.*, A Practical Approach Based on FT-IR Spectroscopy for Identification of Semi-Synthetic and Natural Celluloses in Microplastic Investigation, *Science of the Total Environment, 669* (2019), June, pp. 692-701
[20] Beekes, M., *et al*., Analytical Applications of Fourier Transform-Infrared (FT-IR) Spectroscopy in Microbiology and Prion Research, *Veterinary Microbiology, 123* (2007), 4, pp. 305-319
[21] Li, X., *et al*., Decomposition Kinetic Characteristics of Calcium Carbonate Containing Organic Acids by TGA, *Arabian Journal of Chemistry*, *10* (2013), Suppl. 2, pp. S2534-S2538
[22] Azizi, K., *et al*., Co-Pyrolysis of Binary and Ternary Mixtures of Microalgae, Wood and Waste Tires through TGA, *Renewable Energy, 142* (2019), Nov., pp. 264-271
[23] Blajet, M. Z., *et al*., ChemInform Abstract: Sulfur-Containing Derivatives from (1R)-(-)-Myrtenal Designed as Chiral Ligands, *ChemInform, 47* (2016), 43
[24] Zhang, W., *et al*., Characterization of a Novel D-Lyxose Isomerase from Thermoflavimicrobium Dichotomicum and its Application for D-Mannose Production, *Process Biochemistry, 83* (2019), Aug., pp. 131-136
[25] Iti, M., *et al*., Enzymatic Assay of D-Mannose from Urine, *Bioanalysis, 10* (2018), 23, pp. 1947-1954

[26] Sun, C., *et al*., Inhibitory Effects of Furfural and Vanillin on Two-Stage Gaseous Biofuel Fermentation, *Fuel, 252* (2019), Sept., pp. 350-359
[27] Eversfield, P., *et al*., Selective Oxidation of O-Xylene to Phthalic Anhydride on Tungsten, Tin, and Potassium Promoted VO x on TiO_2 Monolayer Catalysts, *Catalysis Today, 333* (2019), Aug., pp. 120-126
[28] Wang, X., *et al*., Effect of Peroxydisulfate on the Degradation of Phenol Under Dielectric Barrier Discharge Plasma Treatment, *Chemosphere*, *232* (2019), Oct., pp. 462-470
[29] Qin, Z., *et al*., Rapid One-Pot Microwave-Hydrothermal Synthesis of OMS-2 and Full-Solar-Spectrum Photocatalytic Performance for High Phenol Concentration, *Materials Letters, 253* (2019), Oct., pp. 26-29
[30] Ercoli, M., *et al*., Cu/SiO_2: A Step Forward in the Heterogenization of the 2,6-Dimethyl-Phenol Polymerization Catalytic System, *Journal of Molecular Catalysis. A, Chemical*, *204-205* (2003), Sept., 729-735
[31] Khalique, C. M., *et al*., Travelling Waves and Conservation Laws of a (2+1)-Dimensional Coupling System with Korteweg-de Vries Equation, *Applied Mathematics & Nonlinear Sciences, 3* (2018), 1, pp. 241-254
[32] Hosamani, S. M., *et al*., Qspr Analysis of Certain Graph Theocratical Matrices and Their Corresponding Energy, *Applied Mathematics & Nonlinear Sciences, 2* (2017), 1, pp. 131-150
[33] Gutmann, B., *et al*., Homogeneous Liquid-Phase Oxidation of Ethylbenzene to Acetophenone in Continuous Flow Mode, *Acs Catalysis, 3* (2016), 12, pp. 2669-2676
[34] Ba, H., *et al*., Macroscopic Nanodiamonds/β-SiC Composite as Metal-Free Catalysts for Steam-Free Dehydrogenation of Ethylbenzene to Styrene, *Applied Catalysis A General, 499* (2015), June, pp. 217-226
[35] Yoshimura, Y., Reaction of 3-Methyl Phenol with Tung Oil, *Journal of Applied Polymer Science, 28* (2010), 3, pp. 1147-1158
[36] Wang, W. X., *et al*., Dealkylation of 6-Tert-Butyl-3-Methyl-Phenol to m-Cresol, *Petrochemical Technology, 41* (2012), 1, pp. 62-65
[37] Kuendig, E. P., *et al*., ChemInform Abstract: Bicyclo(4.2.0)octa-1,3,5-triene: 2-Mono- and 2,5-Disubstituted Derivatives via Highly Regioselective Lithiation of Its Cr(CO)3 Complex and via Reductive Silylation/Oxidation, *Cheminform, 22* (2010), 3, p. 282
[38] Ujike, K., *et al*., First Detection of 7,8-diazabicyclo[4.2.0]octa-1,3,5-triene Produced from 3,5-cyclohexadiene-1,2-diimine in an Argon Matrix, *Chemical Physics Letters, 396* (2004), 4-6, pp. 288-292
[39] Sugden, D., *et al*., Controlled Release from Solid Pharmaceutical Formulations of two Nalkanoyl- 4-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-ethanamines with Melatoninergic Activity, *Letters in Drug Design & Discovery, 12* (2015), 4, pp. 259-262

Paper submitted: June 5, 2019
Paper revised: August 8, 2019
Paper accepted: September 19, 2019