Computational studies on Emodin (C$_{15}$H$_{10}$O$_5$) from Methanol extract of Pteridium aquilinum leaves

M. E. Khan$^a$, E. E. Etim$^b$, V. J. Anyam$^c$, A. Abel$^d$, I. G. Osigbemhe$^e$, C. T Agber$^f$

$^a$Department of Chemistry, Federal University Lokoja, Kogi State, Nigeria
$^b$Department of Chemical Science, Federal University Wukari Taraba State Nigeria
$^c$Department of Chemistry University of Agriculture Makurdi, Benue State Nigeria
$^d$Department of Pure and Applied Chemistry, Adamawa State University, Mubi, Adamawa State Nigeria
$^e$Department of Industrial Chemistry, Federal University Lokoja, Kogi State, Nigeria
$^f$Department of Chemistry, Benue State University, Makurdi, Benue State, Nigeria

Abstract

This research isolated, characterized, and studied the computational and frequency calculations of emodin, extracted from the leaf extract of Pteridium aquilinum using methanol. Vacuum liquid and tin layer Chromatographic techniques were used for the purification of the molecule. The (VLC purified), fraction was analyzed by Nuclear magnetic resonance (NMR) and the chemical structure of the compound isolated (anthraquinone), was confirmed by $^1$H & $^{13}$C-NMR analyses as emodin (C$_{15}$H$_{10}$O$_5$).

Computational and frequency studies were done on the isolated molecule. Optimized geometry, IR frequencies, Bond distances (R) and angles (A), Dipole moments and other parameters have been computationally determined for the isolated molecule from quantum chemical calculations using the GAUSSIAN 09 retinue programs. Experimentally determined and computationally measured IR frequencies agreed perfectly with each other. Computational studies have been used to predict unobserved chemical phenomena like design of new drugs and materials such as the positions of constituent atoms in relationship to their relative and absolute energies, electronic charge densities, dipoles, higher multiple moments, vibrational frequencies, relativity or other spectroscopic quantities and cross sections for collision with other molecules. This is the first time this anthraquinone, [emodin], with most of the parameters examined is reported from P. aquilinum.

DOI:10.46481/jnsps.2021.301

Keywords: Pteridium aquilinum, Isolated & characterized, Chromatography, Emodin, Optimized geometry, Computational and frequency studies.

Article History:
Received: 14 July 2021
Received in revised form: 14 October 2021
Accepted for publication: 01 November 2021
Published: 29 November 2021

©2021 Journal of the Nigerian Society of Physical Sciences. All rights reserved.
Communicated by: B. J. Falaye
1. Introduction

The phenomenon of screening plants for the presence of phyto-molecules of medicinal importance is common place. Natural products have pharmaceutical / pharmacological activity that are useful in treating diseases and are the starting points for drugs discovery from which synthetic drug analogues can be prepared with improved efficacy, potency, safety and purity [1], when isolated, synthetic strategies and tactics are used by organic Chemists providing challenging mechanisms that permit the biologically active product to the target site. A review reported that 577 plant species have been used traditionally due to the secondary metabolites in them, [2 & 3]. Africa is blessed with its natural pharmacy of variety of plants. Chemists take the pain to analyse these plants’ secondary metabolites for the benefit of mankind as they are precursors for modern drugs, [4].

Based on this concept and theory, the optimal geometry of the eagle fern was calculated. Pteridium aquilinum, brake or common bracken, also known as “eagle fern,” is a species of fern occurring in temperate and subtropical regions in both hemispheres. The extreme lightness of its spores has led to its global distribution, [5]. The large, roughly triangular fronts of the fern are herb-like rhizomes produced singly, arising upwards from an underground, and grow to 1 – 3 m (3 –10 ft) tall; the main stem, or stipe is up to 1 cm (0.4 in) diameter at the base. It is an adaptable plant, which readily colonies disturbed areas. It is a vascular plant that reproduces via spores and has neither seeds nor flowers. It differs from moss by being vascular and it’s of the class Polypodiopsidae. They are the best house purifying plants with their evergreen leaves that help rid the home of harmful toxins and improve humanity by helping to restore moisture to air naturally and also combat winter dryness by raising indoor humidity. They are used as cooked vegetable in Baffousam (Cameroon) and consume with Vernonia amygdalina, Delile and triumfetta rhomboideae. When soaked in wood ash for 24 – 36 hours, free tannic acids are removed and the crosiers consumed and sold as “warabi” or “zenmai in Japan. Rhizomes are consumed in France, Madagascar, and the Canary Island and also used as starch and confections. Leaves are used as straw and bedding for cattle, also to filter oil and palm wine. In Cote d’Ivoire, powdered crosiers are applied to wounds and also as enema to overcome sterility in women. The rhizomes are mixed with Zingiber officinal in juice form and taken as aphrodisiac and with others to calm mental disability. In China, water soaked leaves are used as pesticides. The ash used in Europe for glass and soap production, [6].

Studies carried on Pteridium aquilinum included, potential and historical uses for braken (L) Kuhn, in organic agriculture where the braken were considered a serious weed species, due to toxic constituents and negativity on agriculture and conservation, [7]. The resistance of P. aquilinum (L)Kuhn, to insect attack by Trichoplusia ni (Hubn) where dried braken leaf meals and extracts of the leaf was incorporated into an artificial diet for trichoplusia ni larvae and studied, [8]. Isolation and characterization of the bio assay active molecule(s) from the extract of the leaves of Pteridium aquilinum using the aqueous and methanolic leaf extracts was carefully examined and the extracts used in boosting some female rats hormones, [2]. The plant has many chemical compounds such as emodin, quercetin, shikimic acid, prunasin, ptaquiloside and a ‘bleeding factor’ of other known and unknown structures [9].

Almost every health challenge in the world has a solution in natural products. Thus, the discovery of pharmaceutical drugs remains one of the preeminent tasks in biomedical and related research areas. Advances in science and technology coupled with the development of quantum chemistry, new computational models and software including user-friendly interfaces have reduced the barriers to the application of computational tools in the discovery and structure elucidation of natural products. Consequently, the use of computational chemistry software as a tool to discover and determine the structure of natural products has become more common in recent years. There are several reports of recent studies where computational chemistry is applied to facilitate the discovery and structure elucidation of various natural products with the view to giving insights about the isolated compounds, [10, 11, 12, 13 & 14].

Computational studies are based on quantum mechanics and basic physical constants, with involvement of approximations, but tractable; thus, help find entirely new chemical objects. They are used to find a starting point for a laboratory synthesis or to assist in understanding experimental data such as position and source of spectroscopic peaks and to predict the possibility of entirely unknown molecules or to explore reaction mechanisms not readily studied via experiments. This work is thus, designed to carry out the characterization and identification of bioactive compounds from P. aquilinum leaf extracts and the quantum chemical calculations are employed to further scrutinised and give a better insight about the isolated molecule for the enhancement of human life.

2. Materials and Methods

2.1. Sample Collection and Authentication

Leaves of P. aquilinum that were still green but matured, were collected in and around Michika L. G. A, Adamawa State on 28th July 2014. Authentication of the plant species was by [15], in the State Ministry of Forestry, Mubi North LGA, Adamawa State and a specimen of the plant was kept in their Herbarium. The Forestry Herbarium Index number (FHI) is 1030.

2.2. Preparation of the plant Sample

Leaves of the plant were properly washed with running tap water to avoid dust and other unwanted materials that most have accumulated on the leaves from their natural habitat. Then, dust free leaves were kept to dry under shade in the Chemistry laboratory of Adamawa State University Mubi. These dried leaves were pulverized by using mortar and pestle. Finally, fine powder was obtained from the pulverized leaves by sieving through the kitchen strainer and used for extraction.

---

*Email address: emmaetim@gmail.com (E. E. Etim)*
2.3. Successive Extractions using Microwave Assisted Extraction (MAE)

250g of the powdered sample was poured into a glass (2.5 L) and 500cm³ of normal-hexane was added to it. The bottle was then put into the microwave set at defrost every 3 minutes and removed and cooled. This was repeated 10 times. After filtration, the residues were further extracted similarly using ethyl acetate followed by methanol, [16], and the yields thus: N-hexane, 10g, ethyl acetate, 15g and methanol, 28g respectively.

2.4. Vacuum Liquid Chromatography (VLC)

15g of the methanol extract was dissolved and mixed with celite and left to dry. The dried mixture was then loaded on the VLC that had already been packed with silica gel. It was then rinsed 20 times with 20 cm³ each of n-hexane and ethyl acetate. Ethyl acetate - methanol gradient was used to elute the column and 60 fractions collected.

2.5. Thin Layer Chromatography

TLC was carried out on all the fractions using a solvent gradient system of 9:1 v/v chloroform in methanol. Fractions 12-19 were combined and allowed to dry. The dried sample was then dissolved in methanol but yellow crystals were left undissolved. This was carefully washed. A yellow component was thus purified, spotted on the TLC plate and was labelled (F1), [17]

2.6. Sephadex column

Dissolved components of fractions 12-19, were put on a column loaded with Sephadex and eluted with solvent gradient system of 1:3 v/v methanol, chloroform and ethyl acetate. Seven (7) fractions of 2 cm³ each were collected and spotted on the TLC plate labelled (a) and (b)

2.7. Analysis with Nuclear Magnetic Resonance (NMR) Machine

Fraction (a), RF: 0.65, of the VLC, (with a yellow colour) that was purified with the Sephadex column was sent for NMR analyses. The NMR spectra were run at SIPBS, University, Strathclyde, Glasgow, United Kingdom on JEOL-LA-400 MHz FT-NMR spectrophotometer. [2]

2.8. Quantum Chemical Calculations

Current advances in theoretical and computational thermodynamics have made it easier to study systems, molecular interactions, reactions and predict parameters which would have been experimentally impossible or very difficult to study. The GAUSSIAN 09 retinue of programs was used for all the quantum chemical calculations reported here. The molecule was optimized at the M06-2X level of theory with the 6-31g (d,p) 6-31+G* basis set. The M06-2X functional is a high-non-local functionality with double amount of nonlocal exchange (2X). The optimized structure was stable with real frequencies as shown from the frequency calculations [18, 19, 20, 22-26].

3. Results and Discussion

Detailed computational and frequency studies of the molecule were done and all thermodynamic parameters investigated. This could help to properly identify and justly place the molecule in its chemical context and use it adequately in bioactivity studies and for some bioassays in researches. These investigations and detail analyses were carried out with the aid of Chromatography (VLC, TLC and Sephadex) and other available spectroscopic techniques like Nuclear magnetic resonance (NMR) (1H & 13C-NMR). The computational and frequency studies were carried out using GAUSSIAN 09 retinue programs thus; Levels of theory set: HF/6-311G, Charge = 0, Multiplicity = 1, Stoichiometry C15H10O5, Framework group C1[X(C15H10O5)], Deg. of freedom: 84, Full point group : C1, Largest Abelian subgroup : C1. Largest concise Abelian subgroup: C1, Van-Der-Waals spheres, IR & Raman spectra, Bond distances (R) and angles (A), Dipole moments; field –independent basis (Debye), Rotational constants, HOMO-LUMO structures, Molecular Orbital levels and the Band gaps of: 0.33925 were investigated to bring the structural definition of the molecule, as ‘emodin’

Qualitative TLC, results of P. aquilinum leaf extract (Table 1), performed on the methanol crude extracts are presented and discussed. The two spots detected on the TLC plate of the sephadex column fraction; yellow colour, implied that there are two different components in the extract. Retention factor (Rf) = distance travelled by the solution/ distance travelled by the solvent front; Rf (Fa) = 2.2/3.7 = 0.59 and Rf (Fb) = 2.5/3.7 = 0.68.

| Extract   | No. of spots | Rf     | Quantity |
|-----------|--------------|--------|----------|
| leaf      | 1            | 2.2/3.7=0.59 | 0.5mg    |
| leaf      | 1            | 2.5/3.7=0.68 | (small)  |

3.1. Optimized Geometry

Figure 1, portrays the optimized geometry of P. aquilinum isolated from the methanol extract.

Optimized geometry of P. aquilinum, (Figure 1), obtained at the M062x/6-31g (d,p) level of theory and the Van-Der-Waals sphere (Figure 2), are representations of emodin illustrating where a surface might reside for the molecule based on the hard cutoffs of Van-Der-Waals radii for the individual atoms making up the molecule. [12]

3.2. FTIR Spectra Data for Isolated Emodin

The FTIR spectrum displayed C-OH stretching hydroxyl groups at 3500cm⁻¹, C-H asymmetric stretching in -CH3 at 2925 cm⁻¹, -CH2- stretching frequency at 2900 cm⁻¹, -C=O asymmetric stretching in Carbonyl at 1750, and C-H bending in CH3 at 1400 cm⁻¹. FTIR analysis of isolated emodin is presented in Table 2 and it also attested to the IR spectrum of the computationally obtained levels at the M062x/6-31g (d, p) of the molecule.
Table 2. The FTIR Spectral Data and Interpretation of Isolated methanol extract

| Frequency range cm⁻¹ | Vibrational mode       | Remarks   |
|-----------------------|------------------------|-----------|
| 3500                  | C–OH stretching        | Hydroxyl  |
| 2925                  | C-H-Asymmetric stretching | -CH3     |
| 2900                  | C-H Stretching frequencies | -CH2-   |
| 1750                  | C=O Stretching          | Carbonyl  |
| 1400                  | C-H Bending             |           |

All the major peaks obtained experimentally are in consonance with those obtained computationally at the M062x/6-31g (d, p) level. This further validates both the experimental and computational results. The frequency from 8cm⁻¹ to 3902cm⁻¹ and the corresponding intensity for the IR spectrum obtained at the M062x/6-31g (d, p) level are supporting information. Regarding microwave (or rotational) spectroscopy, this molecule is active with a total dipole moment of 3.7801 Debye obtained at the M062x/6-31g (d, p) level, Table 7. Also, its microwave spectrum has been measured. As an asymmetric top molecule with three different moments of inertia corresponding to the three principal axes, this molecule is expected and it has three different rotational constants. At the M062x/6-31g (d,p) level, the rotational constants obtained for the molecule are 0.7462698, 0.2467690 and 0.1856618 GHz corresponding to the A, B and C rotational constants respectively, Table 8.

Figure 3 portrays the IR spectrum of emodin obtained at the M062x/6-31g (d, p) level of theory. ¹H NMR and ¹³C NMR Spectra interpretation for methanol extract.

¹H NMR of the sample (Table 3) contains; 4 sets of aromatic peaks (7.53, 7.23, 7.12 and 6.62), two sets of phenolic peaks (12.12 and 12.06 ) and one set of methyl groups (2.38, attached to aromatic ring) protons.

¹³C NMR chemical shift values (Table 4) revealed the presence of; 12 aromatic peaks (166.2, 164.9, 161.8, 148.7, 135.7, 133.4, 124.6, 121.0, 113.9, 109.5, 108.5 and 108.4), 2 carboxyls.
(190.7 and 182.2) and methyl (22.0, benzylic) carbons. This inferred that there were two aromatic nuclei that were joined through two carbonyl carbons. Thus, an anthraquinone. It can be suggested again that one of the aromatic nuclei of this anthraquinone contains a methyl and a hydroxyl substituent and the other contains two, hydroxyl substituents, one at position 8 and the other at 6.

Using 2D NMR spectra Correlation (COSY), Heteronuclear Single Quantum Correlation (HSQC) and Heteronuclear Multiple Bonds Correlation (HMBC), emodin was identified as (1, 6, 8-trihydroxy-3-methylemodin), which is an anthraquinone. Both 1D and 2D NMR spectra and also a comparison of the structure of the isolated molecule with literature values of same compound isolated from other plants like *Rumex japonica*, further confirmation was alluded to [21, 12 &13].

### Table 3. $^1$H NMR (400 MHz, DMSO solvent)

| Position | Chemical shift ($\delta$) ppm (J in Hz) | Multiplicity |
|----------|----------------------------------------|--------------|
| 1        | -                                      | -            |
| 2        | 7.20                                   | 1H, m        |
| 3        | -                                      | -            |
| 4        | 7.53 (1.57)                            | 1H, d        |
| 5        | 6.62 (2.40)                            | 1H, d        |
| 6        | -                                      | -            |
| 7        | 7.14 (2.39)                            | 1H, d        |
| 8        | -                                      | -            |
| 9        | -                                      | -            |
| 10       | -                                      | -            |
| 11       | -                                      | -            |
| 12       | -                                      | -            |
| 13       | -                                      | -            |
| 14       | -                                      | -            |
| 3-CH$_3$ | 2.43                                   | 3H, s        |
| 1-OH     | 2.06                                   | 1H, s        |
| 8-OH     | 12.12                                  | 1H, s        |
| 6-OH     | 11.30                                  | 1H, s        |

### Table 4. $^{13}$C NMR Result (DMSO)

| Position | Chemical shift ($\delta$) | Type of C |
|----------|---------------------------|-----------|
| 1        | 161.8                     | C         |
| 2        | 124.6                     | CH        |
| 3        | 148.7                     | C         |
| 4        | 121.0                     | CH        |
| 5        | 108.4                     | CH        |
| 6        | 166.2                     | C         |
| 7        | 109.5                     | CH        |
| 8        | 164.9                     | C         |
| 9        | 190.7                     | C         |
| 10       | 182.2                     | C         |
| 11       | 113.9                     | C         |
| 12       | 133.4                     | C         |
| 13       | 108.5                     | C         |
| 14       | 135.7                     | C         |
| 3-CH$_3$ | 22.0                      | CH$_3$    |

$^1$H and $^{13}$C (NMR) of the spectra were recorded on NMR machine: JEOL-LA-400 MHz FT-NMR spectrophotometer, at SIPBS, University, Strathclyde, Glasgow, United Kingdom, using deuterated solvents as indicated by Tables 3 and 4.

### 3.3. Bond Distances and Bond Angles

Figure 4 is the optimized geometry of Emadin showing the atomic numbers. These numbers help in determining the
distance between two atoms (say atoms 3 and 5) and the angles between atoms. **Table 6** of the supporting information contains the complete bonds distances (in Angstrom) and bond angles (in degrees), of Emodin isolated from the methanol extract.

### 3.4. Homo- Lumo Diagram

Here electron flow, shows whether there is constructive overlap / bonding interaction, or not, between the orbital of the HOMO and those of the LUMO. It also indicates that the orbitals are either occupied or unoccupied, **Table 9** and **Figure 5**. When the overlap is favourable, electron movement is symmetry allowed. The computational calculations have validated the theory of this interaction.

### 3.5. Raman Spectra

This provided good information about the structure of emodin. In this write up, the phase and the polymorphy, crystalline and molecular interactions of the atoms were computed and they tallied with the theory. (See **Figure 6** and **Table 10**).

**Table 5:** IR Values (Frequencies: \(\text{cm}^{-1}\) and their intensities)

| Frequency, \(\text{cm}^{-1}\) | IR Intensity |
|------------------------------|--------------|
| 40.5889                      | 1.7505       |
| 58.1541                      | 0.1401       |
| 72.4885                      | 0.1147       |
| 123.9918                     | 3.1669       |
| 152.1424                     | 2.1859       |
| 180.5744                     | 0.4699       |
| 185.0588                     | 1.6663       |
| 255.505                      | 3.307        |
| 256.5763                     | 0.0736       |
| 277.7802                     | 4.6633       |
| 294.7906                     | 0.2492       |
| 297.6356                     | 2.5751       |
| 351.015                      | 0.4827       |
| 366.8926                     | 1.6488       |
| 382.5217                     | 190.7134     |
| 400.1286                     | 9.5094       |
| 420.2978                     | 0.9179       |
| 464.6792                     | 34.443       |
| 477.8178                     | 16.8814      |
| 505.9458                     | 1.3444       |
| 520.2946                     | 9.4524       |
| 557.7997                     | 4.895        |
| 605.0876                     | 14.3639      |
| 606.812                      | 13.8679      |
| 613.2264                     | 0.8377       |
| 652.8296                     | 4.129        |
| 665.3268                     | 23.4006      |
| 686.8013                     | 28.6752      |
| 701.3117                     | 10.2161      |
| 717.2705                     | 0.6281       |
| 737.3912                     | 2.1851       |
| 744.8034                     | 9.2651       |
| 772.1549                     | 283.7709     |
| 786.5867                     | 5.1204       |
| 806.2587                     | 84.9909      |
| 844.6811                     | 86.8029      |
| 845.4904                     | 24.5256      |
| 949.8981                     | 67.5742      |

*Continued on next page*
### Table 5 – Continued from previous page

| Frequency, cm$^{-1}$ | IR Intensity |
|---------------------|--------------|
| 980.7929            | 33.8411      |
| 991.5636            | 66.5423      |
| 1008.3375           | 5.9754       |
| 1019.5568           | 2.2067       |
| 1063.7093           | 1.3686       |
| 1087.4272           | 13.171       |
| 1110.4729           | 52.0946      |
| 1138.1731           | 32.1339      |
| 1196.3708           | 5.8936       |
| 1205.8194           | 206.5051     |
| 1230.0187           | 7.0492       |
| 1253.0616           | 123.2033     |
| 1291.437           | 224.8896     |
| 1294.8107           | 424.9948     |
| 1311.5505           | 92.2745      |
| 1348.5262           | 102.8252     |
| 1393.5713           | 71.2756      |
| 1400.046            | 119.8228     |
| 1440.4723           | 349.6365     |
| 1449.158            | 118.6796     |
| 1486.7681           | 127.3453     |
| 1504.6975           | 67.6164      |
| 1515.7165           | 664.1199     |
| 1563.6894           | 1.0644       |
| 1577.6142           | 7.1853       |
| 1599.795            | 7.4221       |
| 1627.5681           | 97.4458      |
| 1640.3534           | 10.8432      |
| 1642.8372           | 63.6547      |
| 1660.0202           | 41.9661      |
| 1725.1233           | 26.9024      |
| 1743.1457           | 155.4465     |
| 1779.4404           | 42.6281      |
| 1800.8258           | 161.4526     |
| 1805.9447           | 688.232      |
| 1858.3537           | 0.0332       |
| 3168.3115           | 25.498       |
| 3223.758            | 22.4323      |
| 3253.8947           | 25.0516      |
| 3375.7378           | 3.6376       |
| 3377.4741           | 1.6247       |
| 3378.858            | 5.0178       |
| 3411.1628           | 0.2215       |
| 3907.6476           | 236.8743     |
| 3914.4907           | 145.2159     |
| 4084.1357           | 117.2641     |

---

**Structural illustrations of Bond Distance and Bond Angles**

Table 6: Numerical values of bond distances and Angles

| R(1-2)  | 1.405 |
|---------|-------|

Continued on next page
|   |   |
|---|---|
| R(1-8) | 1.387 |
| R(1-9) | 1.349 |
| R(2-3) | 1.457 |
| R(2-4) | 1.405 |
| R(3-7) | 1.460 |
| R(3-20) | 1.251 |
| R(4-5) | 1.487 |
| R(4-9) | 1.373 |
| R(5-6) | 1.482 |
| R(5-10) | 1.221 |
| R(6-7) | 1.410 |
| R(6-11) | 1.370 |
| R(7-12) | 1.395 |
| R(8-18) | 1.374 |
| R(8-21) | 1.066 |
| R(9-18) | 1.395 |
| R(9-22) | 1.069 |
| R(10-14) | 1.405 |
| R(10-15) | 1.069 |
| R(12-13) | 1.396 |
| R(12-16) | 1.352 |
| R(13-14) | 1.375 |
| R(13-17) | 1.069 |
| R(14-27) | 1.505 |
| R(16-25) | 0.954 |
| R(18-23) | 1.364 |
| R(19-24) | 0.954 |
| R(23-26) | 0.946 |
| R(27-28) | 1.082 |
| R(27-29) | 1.082 |
| R(27-30) | 1.079 |
| R(20-24) | 1.828 |
| R(20-25) | 1.834 |
| A(2-1-8) | 120.5 |
| A(2-1-19) | 123.3 |
| A(1-2-3) | 121.1 |
| A(1-2-4) | 118.2 |
| A(7-19-1) | 119.5 |
| A(1-8-21) | 119.5 |
| A(1-19-24) | 113.6 |
| A(3-2-4) | 120.7 |
| A(2-3-7) | 119.6 |
| A(2-3-20) | 120.2 |
| A(2-4-5) | 120.3 |
| A(2-4-9) | 121.4 |
| A(7-3-20) | 120.1 |
| A(3-7-6) | 120.8 |
| A(3-7-12) | 121.1 |
| A(3-20-24) | 105.4 |
| A(3-20-25) | 105.5 |
| A(5-4-9) | 118.3 |
| A(4-5-6) | 118.4 |

**Table 6 – Continued from previous page**
Table 6 – Continued from previous page

| A(4-5-10) | 120.4 |
| A(4-9-18) | 119.1 |
| A(4-9-22) | 119.4 |
| A(6-5-10) | 121.2 |
| A(5-6-7)  | 120.1 |
| A(5-6-11) | 118.8 |
| A(7-6-11) | 121.1 |
| A(6-7-12) | 118.1 |
| A(6-11-14)| 120.5 |
| A(6-11-15)| 118.9 |
| A(7-12-13)| 120.2 |
| A(7-12-16)| 123.9 |
| A(18-8-21)| 120.7 |
| A(8-18-9 )| 121.1 |
| A(8-18-23)| 117.2 |
| A(18-9-22)| 121.5 |
| A(9-18-23)| 121.7 |
| A(14-11-15)| 120.6 |
| A(11-14-13)| 118.7 |
| A(11-14-27)| 119.9 |
| A(13-12-16)| 115.9 |
| A(12-13-14)| 121.3 |
| A(12-13-17)| 117.1 |
| A(12-16-25)| 113.5 |
| A(14-13-17)| 121.6 |
| A(13-14-27)| 121.4 |
| A(14-27-28)| 110.8 |
| A(14-27-29)| 110.8 |
| A(14-27-30)| 111.4 |
| A(16-25-20)| 135.9 |
| A(18-23-26)| 115.2 |
| A(19-24-20)| 136.3 |
| A(28-27-29)| 107.5 |
| A(28-27-30)| 108.1 |
| A(29-27-30)| 108.1 |
| A(24-20-25)| 149.1 |
| W1(A)     | 40.6  |
| W2(A)     | 58.2  |
| W3(A)     | 72.5  |
| W4(A)     | 124.0 |
| W5(A)     | 152.1 |
| W6(A)     | 180.6 |
| W7(A)     | 185.1 |
| W8(A)     | 255.5 |
| W9(A)     | 256.6 |
| W10(A)    | 277.8 |
| W11(A)    | 294.8 |
| W12(A)    | 297.6 |
| W13(A)    | 351.0 |
| W14(A)    | 366.9 |
| W15(A)    | 382.5 |
| W16(A)    | 400.1 |
| W17(A)    | 420.3 |

Continued on next page
| W18(A)  | 464.7 |
|---------|-------|
| W19(A)  | 477.8 |
| W20(A)  | 505.9 |
| W21(A)  | 520.3 |
| W22(A)  | 557.8 |
| W23(A)  | 605.1 |
| W24(A)  | 606.8 |
| W25(A)  | 613.2 |
| W26(A)  | 652.8 |
| W27(A)  | 665.3 |
| W28(A)  | 686.8 |
| W29(A)  | 701.3 |
| W30(A)  | 717.3 |
| W31(A)  | 737.4 |
| W32(A)  | 744.8 |
| W33(A)  | 772.2 |
| W34(A)  | 786.6 |
| W35(A)  | 806.3 |
| W36(A)  | 844.7 |
| W37(A)  | 845.5 |
| W38(A)  | 949.9 |
| W39(A)  | 980.8 |
| W40(A)  | 991.6 |
| W41(A)  | 1008.3|
| W42(A)  | 1019.6|
| W43(A)  | 1063.7|
| W44(A)  | 1087.4|
| W45(A)  | 1110.5|
| W46(A)  | 1138.2|
| W47(A)  | 1196.4|
| W48(A)  | 1205.8|
| W49(A)  | 1230.0|
| W50(A)  | 1253.1|
| W51(A)  | 1291.4|
| W52(A)  | 1294.8|
| W53(A)  | 1311.6|
| W54(A)  | 1348.5|
| W55(A)  | 1393.6|
| W56(A)  | 1400.0|
| W57(A)  | 1440.5|
| W58(A)  | 1449.2|
| W59(A)  | 1486.8|
| W60(A)  | 1504.7|
| W61(A)  | 1515.7|
| W62(A)  | 1563.7|
| W63(A)  | 1577.6|
| W64(A)  | 1599.8|
| W65(A)  | 1627.6|
| W66(A)  | 1640.4|
| W67(A)  | 1642.8|
| W68(A)  | 1660.0|
| W69(A)  | 1725.1|
| W70(A)  | 1743.1|
Table 6 – Continued from previous page

| W71(A) | 1779.4 |
|--------|--------|
| W72(A) | 1800.8 |
| W73(A) | 1805.9 |
| W74(A) | 1858.4 |
| W75(A) | 3168.3 |
| W76(A) | 3223.8 |
| W77(A) | 3253.9 |
| W78(A) | 3375.7 |
| W79(A) | 3377.5 |
| W80(A) | 3378.9 |
| W81(A) | 3411.2 |
| W82(A) | 3907.6 |
| W83(A) | 3914.5 |
| W84(A) | 4084.1 |

Table 7. Dipole moment (Field–independent Basis, Debye)

| X    | 1.9607 |
| Y    | -3.2319 |
| Z    | -0.0025 |
| Total| 3.7801 |

Table 8. Rot. Constants for Emodin

| Rotational Constants | GHZ  |
|----------------------|------|
| A                    | 0.7462698 |
| B                    | 0.2467690 |
| C                    | 0.1856618 |

Table 9: Numerical indicators of occupied and unoccupied molecular orbitals

| 1 Occupied         | -20.6106 |
|--------------------|----------|
| 2 Occupied         | -20.59061 |
| 3 Occupied         | -20.58999 |
| 4 Occupied         | -20.58463 |
| 5 Occupied         | -20.58063 |
| 6 Occupied         | -11.39494 |
| 7 Occupied         | -11.38389 |
| 8 Occuped          | -11.35976 |
| 9 Occuped          | -11.3571 |
| 10 Occuped         | -11.35506 |

Continued on next page
| Occupied | Value   |
|----------|---------|
| 11       | -11.30275 A |
| 12       | -11.29346 A |
| 13       | -11.29192 A |
| 14       | -11.28269 A |
| 15       | -11.28221 A |
| 16       | -11.26999 A |
| 17       | -11.2639 A |
| 18       | -11.26076 A |
| 19       | -11.25788 A |
| 20       | -11.24752 A |
| 21       | -1.45133 A |
| 22       | -1.443 A |
| 23       | -1.43897 A |
| 24       | -1.43163 A |
| 25       | -1.4124 A |
| 26       | -1.21648 A |
| 27       | -1.19863 A |
| 28       | -1.12143 A |
| 29       | -1.07739 A |
| 30       | -1.06499 A |
| 31       | -1.05973 A |
| 32       | -0.9952 A |
| 33       | -0.9526 A |
| 34       | -0.92195 A |
| 35       | -0.89005 A |
| 36       | -0.86663 A |
| 37       | -0.83926 A |
| Occupied | 38 | -0.79888 | A |
| Occupied | 39 | -0.77404 | A |
| Occupied | 40 | -0.76007 | A |
| Occupied | 41 | -0.73987 | A |
| Occupied | 42 | -0.72586 | A |
| Occupied | 43 | -0.69958 | A |
| Occupied | 44 | -0.69417 | A |
| Occupied | 45 | -0.67067 | A |
| Occupied | 46 | -0.66231 | A |
| Occupied | 47 | -0.65235 | A |
| Occupied | 48 | -0.64739 | A |
| Occupied | 49 | -0.63103 | A |
| Occupied | 50 | -0.62251 | A |
| Occupied | 51 | -0.61638 | A |
| Occupied | 52 | -0.60289 | A |
| Occupied | 53 | -0.60155 | A |
| Occupied | 54 | -0.59301 | A |
| Occupied | 55 | -0.58622 | A |
| Occupied | 56 | -0.58475 | A |
| Occupied | 57 | -0.56457 | A |
| Occupied | 58 | -0.56087 | A |
| Occupied | 59 | -0.55885 | A |
| Occupied | 60 | -0.54681 | A |
| Occupied | 61 | -0.54236 | A |
| Occupied | 62 | -0.53297 | A |
| Occupied | 63 | -0.49741 | A |
| Occupied | 64 | -0.48094 | A |

*Continued on next page*
Table 9 – Continued from previous page

|   |       |      |
|---|-------|------|
| 65| Occupied | -0.46984 |
| 66| Occupied | -0.44326 |
| 67| Occupied | -0.37943 |
| 68| Occupied | -0.36226 |
| 69| Occupied | -0.35055 |
| 70| Occupied | -0.33995 |
| 71| Unoccupied | -0.0007 |
| 72| Unoccupied | 0.06955 |
| 73| Unoccupied | 0.10587 |
| 74| Unoccupied | 0.13378 |
| 75| Unoccupied | 0.13583 |
| 76| Unoccupied | 0.14836 |
| 77| Unoccupied | 0.18701 |
| 78| Unoccupied | 0.2009 |
| 79| Unoccupied | 0.2011 |
| 80| Unoccupied | 0.2037 |
| 81| Unoccupied | 0.21134 |
| 82| Unoccupied | 0.22203 |
| 83| Unoccupied | 0.22495 |
| 84| Unoccupied | 0.23454 |
| 85| Unoccupied | 0.23529 |
| 86| Unoccupied | 0.25213 |
| 87| Unoccupied | 0.32229 |
| 88| Unoccupied | 0.34319 |
| 89| Unoccupied | 0.34611 |
| 90| Unoccupied | 0.35786 |
| 91| Unoccupied | 0.37219 |

Continued on next page
|   |   |   |
|---|---|---|
| 92 | Unoccupied | 0.3831 |
| 93 | Unoccupied | 0.4018 |
| 94 | Unoccupied | 0.40497 |
| 95 | Unoccupied | 0.41765 |
| 96 | Unoccupied | 0.43383 |
| 97 | Unoccupied | 0.44363 |
| 98 | Unoccupied | 0.44626 |
| 99 | Unoccupied | 0.45481 |
| 100 | Unoccupied | 0.46011 |
| 101 | Unoccupied | 0.48707 |
| 102 | Unoccupied | 0.49981 |
| 103 | Unoccupied | 0.50292 |
| 104 | Unoccupied | 0.50877 |
| 105 | Unoccupied | 0.51194 |
| 106 | Unoccupied | 0.52321 |
| 107 | Unoccupied | 0.52819 |
| 108 | Unoccupied | 0.53979 |
| 109 | Unoccupied | 0.54525 |
| 110 | Unoccupied | 0.55944 |
| 111 | Unoccupied | 0.56865 |
| 112 | Unoccupied | 0.57009 |
| 113 | Unoccupied | 0.58434 |
| 114 | Unoccupied | 0.58662 |
| 115 | Unoccupied | 0.59683 |
| 116 | Unoccupied | 0.60621 |
| 117 | Unoccupied | 0.60814 |
| 118 | Unoccupied | 0.61375 |
Table 9 – Continued from previous page

|   | Unoccupied |     |
|---|------------|-----|
| 119 | 0.61988  | A   |
| 120 | 0.62327  | A   |
| 121 | 0.62597  | A   |
| 122 | 0.62776  | A   |
| 123 | 0.63742  | A   |
| 124 | 0.65303  | A   |
| 125 | 0.65887  | A   |
| 126 | 0.66405  | A   |
| 127 | 0.67701  | A   |
| 128 | 0.68162  | A   |
| 129 | 0.68987  | A   |
| 130 | 0.69117  | A   |
| 131 | 0.69598  | A   |
| 132 | 0.7286   | A   |
| 133 | 0.73459  | A   |
| 134 | 0.75046  | A   |
| 135 | 0.75306  | A   |
| 136 | 0.76128  | A   |
| 137 | 0.77724  | A   |
| 138 | 0.77807  | A   |
| 139 | 0.77996  | A   |
| 140 | 0.80091  | A   |
| 141 | 0.80389  | A   |
| 142 | 0.81138  | A   |
| 143 | 0.81625  | A   |
| 144 | 0.82077  | A   |
| 145 | 0.83575  | A   |

Continued on next page
|   |     |     |
|---|-----|-----|
| 146 | Unoccupied | 0.84813 |
| 147 | Unoccupied | 0.86274 |
| 148 | Unoccupied | 0.88017 |
| 149 | Unoccupied | 0.88642 |
| 150 | Unoccupied | 0.88885 |
| 151 | Unoccupied | 0.89606 |
| 152 | Unoccupied | 0.92417 |
| 153 | Unoccupied | 0.93098 |
| 154 | Unoccupied | 0.9795  |
| 155 | Unoccupied | 0.98929 |
| 156 | Unoccupied | 1.01128 |
| 157 | Unoccupied | 1.01814 |
| 158 | Unoccupied | 1.02265 |
| 159 | Unoccupied | 1.02918 |
| 160 | Unoccupied | 1.05372 |
| 161 | Unoccupied | 1.06017 |
| 162 | Unoccupied | 1.06199 |
| 163 | Unoccupied | 1.06346 |
| 164 | Unoccupied | 1.07991 |
| 165 | Unoccupied | 1.08652 |
| 166 | Unoccupied | 1.09138 |
| 167 | Unoccupied | 1.10578 |
| 168 | Unoccupied | 1.11793 |
| 169 | Unoccupied | 1.1187  |
| 170 | Unoccupied | 1.13433 |
| 171 | Unoccupied | 1.14179 |
| 172 | Unoccupied | 1.14713 |

*Continued on next page*
Table 9 – Continued from previous page

|   |   |   |
|---|---|---|
| 173 | Unoccupied | 1.16523 A |
| 174 | Unoccupied | 1.17615 A |
| 175 | Unoccupied | 1.1908 A |
| 176 | Unoccupied | 1.19371 A |
| 177 | Unoccupied | 1.20229 A |
| 178 | Unoccupied | 1.21612 A |
| 179 | Unoccupied | 1.25361 A |
| 180 | Unoccupied | 1.26206 A |
| 181 | Unoccupied | 1.27792 A |
| 182 | Unoccupied | 1.29634 A |
| 183 | Unoccupied | 1.34272 A |
| 184 | Unoccupied | 1.36669 A |
| 185 | Unoccupied | 1.37455 A |
| 186 | Unoccupied | 1.38165 A |
| 187 | Unoccupied | 1.39717 A |
| 188 | Unoccupied | 1.45107 A |
| 189 | Unoccupied | 1.48546 A |
| 190 | Unoccupied | 1.49397 A |
| 191 | Unoccupied | 1.50947 A |
| 192 | Unoccupied | 1.51616 A |
| 193 | Unoccupied | 1.54722 A |
| 194 | Unoccupied | 1.55972 A |
| 195 | Unoccupied | 1.62076 A |
| 196 | Unoccupied | 1.92958 A |
| 197 | Unoccupied | 1.9693 A |
| 198 | Unoccupied | 1.99045 A |
| 199 | Unoccupied | 2.01527 A |

Continued on next page
| No. | Occupancy | Value      |
|-----|-----------|------------|
| 200 | Unoccupied| 2.04241 A  |
| 201 | Unoccupied| 2.47872 A  |
| 202 | Unoccupied| 2.55557 A  |
| 203 | Unoccupied| 2.57245 A  |
| 204 | Unoccupied| 2.58411 A  |
| 205 | Unoccupied| 2.61213 A  |
| 206 | Unoccupied| 2.66724 A  |
| 207 | Unoccupied| 2.67833 A  |
| 208 | Unoccupied| 2.7261 A   |
| 209 | Unoccupied| 2.75184 A  |
| 210 | Unoccupied| 2.76667 A  |
| 211 | Unoccupied| 2.83591 A  |
| 212 | Unoccupied| 2.87279 A  |
| 213 | Unoccupied| 2.87898 A  |
| 214 | Unoccupied| 2.89883 A  |
| 215 | Unoccupied| 2.92545 A  |
| 216 | Unoccupied| 2.94814 A  |
| 217 | Unoccupied| 2.96326 A  |
| 218 | Unoccupied| 2.98075 A  |
| 219 | Unoccupied| 3.03619 A  |
| 220 | Unoccupied| 3.05634 A  |
| 221 | Unoccupied| 3.09158 A  |
| 222 | Unoccupied| 3.09641 A  |
| 223 | Unoccupied| 3.10212 A  |
| 224 | Unoccupied| 3.10332 A  |
| 225 | Unoccupied| 3.10964 A  |
| 226 | Unoccupied| 3.17293 A  |

*Continued on next page*
|   |   |
|---|---|
| 227 | 3.23325 |
| Unoccupied | A |
| 228 | 3.248 |
| Unoccupied | A |
| 229 | 3.29189 |
| Unoccupied | A |
| 230 | 3.30673 |
| Unoccupied | A |
| 231 | 3.32245 |
| Unoccupied | A |
| 232 | 3.34172 |
| Unoccupied | A |
| 233 | 3.35642 |
| Unoccupied | A |
| 234 | 3.35848 |
| Unoccupied | A |
| 235 | 3.37538 |
| Unoccupied | A |
| 236 | 3.37812 |
| Unoccupied | A |
| 237 | 3.38723 |
| Unoccupied | A |
| 238 | 3.41087 |
| Unoccupied | A |
| 239 | 3.46033 |
| Unoccupied | A |
| 240 | 3.48637 |
| Unoccupied | A |
| 241 | 3.502 |
| Unoccupied | A |
| 242 | 3.53895 |
| Unoccupied | A |
| 243 | 3.56422 |
| Unoccupied | A |
| 244 | 3.57188 |
| Unoccupied | A |
| 245 | 3.59923 |
| Unoccupied | A |
| 246 | 3.61431 |
| Unoccupied | A |
| 247 | 3.62728 |
| Unoccupied | A |
| 248 | 3.65106 |
| Unoccupied | A |
| 249 | 3.67652 |
| Unoccupied | A |
| 250 | 3.70142 |
| Unoccupied | A |
| 251 | 3.71733 |
| Unoccupied | A |
| 252 | 3.74714 |
| Unoccupied | A |
| 253 | 3.76852 |
| Unoccupied | A |

*Continued on next page*
|   |   |   |
|---|---|---|
| 254 | 3.89765 | Unoccupied |
| 255 | 3.98257 | Unoccupied |
| 256 | 5.32337 | Unoccupied |
| 257 | 5.35191 | Unoccupied |
| 258 | 5.35493 | Unoccupied |
| 259 | 5.38283 | Unoccupied |
| 260 | 5.40342 | Unoccupied |
| 261 | 5.44518 | Unoccupied |
| 262 | 5.49454 | Unoccupied |
| 263 | 5.50494 | Unoccupied |
| 264 | 5.54169 | Unoccupied |
| 265 | 5.5829  | Unoccupied |
| 266 | 5.60217 | Unoccupied |
| 267 | 5.66417 | Unoccupied |
| 268 | 5.70088 | Unoccupied |
| 269 | 5.73321 | Unoccupied |
| 270 | 5.76144 | Unoccupied |
| 271 | 24.19134 | Unoccupied |
| 272 | 24.27042 | Unoccupied |
| 273 | 24.41848 | Unoccupied |
| 274 | 24.49212 | Unoccupied |
| 275 | 24.49889 | Unoccupied |
| 276 | 24.51616 | Unoccupied |
| 277 | 24.5837  | Unoccupied |
| 278 | 24.63317 | Unoccupied |
| 279 | 24.7082  | Unoccupied |
| 280 | 24.80808 | Unoccupied |
Table 9 – Continued from previous page

|      | Frequency (cm$^{-1}$) | Raman Activity |
|------|----------------------|----------------|
| 281  | 24.81693             | A              |
| 282  | 24.83965             | A              |
| 283  | 24.88602             | A              |
| 284  | 25.00561             | A              |
| 285  | 25.02082             | A              |
| 286  | 51.55558             | A              |
| 287  | 51.58631             | A              |
| 288  | 51.59188             | A              |
| 289  | 51.59641             | A              |
| 290  | 51.60474             | A              |

Band gap: 0.33925 A.U

Table 10: Frequencies cm$^{-1}$ and Raman activities

| Frequency, cm$^{-1}$ | Raman Activity |
|----------------------|----------------|
| 40.5889              | 0.0308         |
| 58.1541              | 0.3493         |
| 72.4885              | 0.0255         |
| 123.9918             | 0.0304         |
| 152.1424             | 0.1427         |
| 180.5744             | 1.7709         |
| 185.0588             | 0.3809         |
| 255.505              | 1.9977         |
| 256.5763             | 1.6381         |
| 277.7802             | 0.0179         |
| 294.7906             | 0.6864         |
| 297.6356             | 0.4601         |
| 351.015              | 6.5213         |
| 366.8926             | 1.5406         |
| 382.5217             | 3.5322         |
| 400.1286             | 2.3964         |
| 420.2978             | 1.913          |
| 464.6792             | 0.0432         |
| 477.8178             | 3.0011         |
| 505.9458             | 35.2839        |
| 520.2946             | 2.4177         |
| 557.7997             | 3.7289         |
| 605.0876             | 23.6777        |
| 606.812              | 1.0858         |
| 613.2264             | 1.5184         |
| 652.8296             | 0.7743         |
| 665.3268             | 0.1479         |
| 686.8013             | 1.8993         |

Continued on next page
| Frequency, cm\(^{-1}\) | Raman Activity |
|--------------------------|----------------|
| 701.3117                 | 0.4288         |
| 717.2705                 | 0.0411         |
| 737.3912                 | 0.1857         |
| 744.8034                 | 0.5408         |
| 772.1549                 | 0.8902         |
| 786.5867                 | 6.7614         |
| 806.2587                 | 0.5934         |
| 844.6811                 | 0.2227         |
| 845.4904                 | 1.5859         |
| 949.8981                 | 0.3197         |
| 980.7929                 | 0.8345         |
| 991.5636                 | 4.1317         |
| 1008.3375                | 1.311          |
| 1019.5568                | 54.1302        |
| 1063.7093                | 0.7049         |
| 1087.4272                | 6.8712         |
| 1110.4729                | 1.8682         |
| 1138.1731                | 3.5729         |
| 1196.3708                | 0.5286         |
| 1205.8194                | 11.7034        |
| 1230.0187                | 26.9241        |
| 1253.0616                | 11.4807        |
| 1291.437                 | 9.0978         |
| 1294.8107                | 18.6095        |
| 1311.5505                | 10.9375        |
| 1348.5262                | 55.9278        |
| 1393.5713                | 7.765          |
| 1400.046                 | 11.0092        |
| 1440.4723                | 195.2705       |
| 1449.158                 | 77.3445        |
| 1486.7681                | 104.1229       |
| 1504.6975                | 44.8716        |
| 1515.7165                | 31.9762        |
| 1563.6894                | 54.3211        |
| 1577.6142                | 15.8238        |
| 1599.795                 | 32.9398        |
| 1627.5681                | 30.8732        |
| 1640.3534                | 21.3528        |
| 1642.8372                | 13.7481        |
| 1660.0202                | 9.3907         |
| 1725.1233                | 85.1739        |
| 1743.1457                | 150.3192       |
| 1779.4404                | 106.9382       |
| 1800.8258                | 151.5551       |
| 1805.9447                | 13.6314        |
| 1858.3537                | 221.7421       |
| 3168.3115                | 226.1542       |
| 3223.758                 | 93.6794        |
| 3253.8947                | 74.8114        |
| 3375.7378                | 45.7586        |
| 3377.4741                | 59.3447        |
| 3378.858                 | 113.9246       |

**Continued on next page**
4. Conclusion

This article is the first to have done complete computational and frequency studies on the isolated anthraquinone, “emodin” from *P. aquilinum*. Optimized geometry, IR frequencies, Bond distances (R) and angles (A), Dipole moments and other parameters have been computationally determined for the isolated molecule from quantum chemical calculations using the GAUSSIAN 09 retinue programs. Experimentally determined and computationally measured IR frequencies agreed perfectly with each other. This can be used to predict unobserved chemical phenomena like design of new drugs and materials such as the positions of constituent atoms, in relationship to their relative and absolute energies, electronic charge densities, dipoles, higher multiple moments, vibrational frequencies, relativity or other spectroscopic quantities and cross sections for collision with other molecules.

Acknowledgments

Our gratitude to Prof J. O. Igoli and SIPBS, University of Strathclyde, Glasgow, UK for their help in the analyses and the Indian Institute of Science, Bangalore for facilitating the computational calculations.

References

[1] S. Samala, & S. Veeresham “Enhanced Bioavailability of Glimipirida in the presence of Boswellic acids in streptozotocin - induced Diabetic Rat model”, Natural Products Chemistry and Research 1 (2013) 166.

[2] M. E. Khan, E. T. Williams, A. Abel & I. Toma “Effects of the aqueous and methanolic leaf extracts of *Pteridium aquilinum* (linnaeus) on some female rats hormones”, Direct Research Journal of Public Health and Environmental Technology 2 (2019). 2016 8.

[3] D. Kumar, A. Kumar & O. J. Prakash “Foliculogenesis and quickening of maturation of the follicle in the pre-ovulatory phase”, Ethnopharmacol 140 (2012) 1.

[4] R. R. Da Silva, P. C. Dorrestein & R. A. Quinn “Illuminating the dark matter in metabolomics”, Proceedings od the National Academy of Sciences of the United States of America 112 (2015) 12549.

[5] J. O. Igoli & S. Neumann “In silico fragmentation for computer assisted identification of metabolite mass spectra”, BMC Bioinformatics 11 (2010) 148.

[6] M. Admu Traditional herbalist verse with medicinal plants of the Mubi and Michika regions of Adamawa State (2016).

[7] J. N. Anyam, T. A. Tor anyiin & J. O. Igoli “Studies on Dacyrodes edullis II: Phytochemical and medicinal principles of boiled seed”, International Journal of Current Research in Chemistry and Pharmaceutical Science 2 (2016) 32.

[8] B. J. Owolabi, O. Iyekoba, G. E. Okpara & H. C. Ndibe “Synthesis, tentative characterization and antimicrobial activities of 1-ethyl 2-methyl-4-nitroimidazole-5-thiol and its derivatives”, Journal of Chemical Society of Nigeria 44 (2019) 355.

[9] E. E. Etim & E. Arunan “Rotational Spectroscopy and Interstellar Molecules, Planex”, News letter 5 (2015) 16.

[10] E. E. Etim, P. Gorai, A. Das, S. Charabati & E. Arunan “Systematic Theoretical Study on the Interstellar Carbon Chain Molecules”, The Astrophysical Journal 832 (2016) 144.

[11] E. E. Etim, P. Gorai, A. Das & E. Runan “C5H9N Isomers: Pointers to Possible Branched Chain Inte rstellar Molecules”, European Physical Journal D 71 (2017) 86.

[12] G. Shuying, B. Feng, Z. Ruoman, M. Jiankang & W. Wei “Preparative isolation of three Anthraquinones from Rumex japonicus by high speed counter-current Chromatography”, Molecules 16 (2011) 1201.
[22] O. A. Ushie, E. E. Etim, H. M. Adamu, I. Y. Chindo, C. Andrew & G. P. Khanal “Quantum Chemical Studies on Decyl Heptadecanoate (C_{27}H_{54}O_{2}) Detected In Ethyl Acetate Leaf Extract of *Chrysophyllum albidium*”, Elixir Applied Chemistry 111 (2017) 48828.

[23] A. I. Onen, J. Joseph, E. E. Etim & N. O. Eddy “Quantum Chemical Studies on the Inhibition Mechanism of Ficus carica, FC and Vitellaria paradoxa, VP Leaf Extracts”, Journal of Advanced Chemical Sciences 3 (2017) 496.

[24] O. A. Ushie, E. E. Etim, A. I. Onen, C. Andrew, U. Lawal & G. P. Khanal “Computational Studies of β-amyrin acetate (C_{32}H_{52}O_{2}) Detected in Methanol Leaf Extract of *Chrysophyllum albidium*”, Journal of Chemical Society of Nigeria 44 (2019) 561.

[25] E. E. Etim, O. E. Godwin, S. A. Olagboye & M. E. Khan “Protonation in Benzyl Alcohol: Different Proton Affinities, Same Neutral Molecule”, Asian Journal of Emergency Research 3 (2021) 19.

[26] E. Etim, O. E. Godwin & S. A. Olagboye “Protonation in Heteronuclear Diatomic Molecules: Same Molecule, Different Proton Affinities”, Communication in Physical Sciences 6 (2020) 835.