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Gloria Ihuoma Ndukwe
Department of Chemistry, Rivers State University of Science and Technology, Nkpolu-Oroworukwo P.M.B. 5080 Port Harcourt, Rivers State, Nigeria

Chukwunonye Moses Ojinnaka
Department of Pure & Industrial Chemistry, University of Port Harcourt, East/West Road P.M.B. 5323 Choba, Rivers State, Nigeria

Adebola Omowumi Oyedeji
Department of Chemical and Physical Sciences, Walter Sisulu University, Private Bag X1, Mthatha 5117 Eastern Cape, South Africa

Correspondence
Chukwunonye Moses Ojinnaka
Department of Pure & Industrial Chemistry, University of Port Harcourt, East/West Road P.M.B. 5323 Choba, Rivers State, Nigeria

Novel bioactive triterpenoid saponin from the fruits of *Napoleonaea imperialis* P. Beauv (Lecythidaceae)

Gloria Ihuoma Ndukwe, Chukwunonye Moses Ojinnaka and Adebola Omowumi Oyedeji

Abstract
Napoleonaea imperialis P. Beauv (Lecythidaceae) is a medicinal plant commonly found in South-Eastern Nigeria. The ripe fruits were extracted and partitioned into hexane, chloroform, n-butanol and aqueous fractions. These fractions were earlier tested and shown to possess anti-bacterial activities. The chloroform extract was chromatographed and purified to give compounds 1-5 whose structures were elucidated using ir, ^{1}H and ^{13}C-nmr as methyl-1,3,5-triene-tricyclopentadecanoate (1); 5-methyl-5-toluyl-3,4,6-trihydropyran-2-one (2, napoleonapyran-2-one); 4-ethoxy-bicyclodecylbenzoate (3); 3β-O-[β-D-glucopyranosyl(1→2)][β-D-glucopyranosyl(1→4)][β-D-glucopyranosyl]-16α,22α,24,28-tetrahydroxy-21-β-O-angeloxyolean-12-ene-29-al (4, napoleon aside -B) and 3-O-[β-D-glucopyranosyl]-1,4–dimethyl-2,4,5,10-tetrahydroxy–bicyclodecane (5).

Keywords: *Napoleonaea imperialis, Lecythidaceae, fruits,* structure, napoleonapyran-2-one, napoleon aside-B

1. Introduction
There are ten species in the genus, *Napoleonaea* [1], but *Napoleonaea imperialis* and *Napoleonaea vogelli* are the most common species found in Southern Nigeria. The bark of *Napoleonaea vogelli* and *Napoleonaea imperialis* are used locally as cough medicine. The seed pulp of some species of *Napoleonaea* is eaten [2]. Different parts of *Napoleonaea imperialis* P. Beauv are used in traditional medicine for treatment of infectious diseases [3, 4]. The chemistry and pharmacology of different species of *Napoleonaea* have been reported [5-11]. In our previous studies, the fruits of *Napoleonaea imperialis* showed great potentials as a molluscicide [12] and anti-bacterial agent [13]. In continuation of our studies, we report the isolation and characterization of novel compounds from the extracts of *Napoleonaea imperialis* that were earlier shown to be bioactive [13].

2. Experimental
2.1 General
The n-butanol, deuterated chloroform, deuterated methanol and deuterated DMSO used for this work were analytical grade. All other solvents used were re-distilled. The NMR spectra were taken on Bruker 600 MHz and Bruker 400 MHz operating at 600.1 MHz and 400.22 MHz for proton and 150.89 MHz and 100.63 MHz for carbon 13 respectively. NMR of pure compounds were processed using Bruker software. All samples were run at 25 °C. NMR spectra were calibrated using solvent signals (^{13}C : $CDCl_3$ 77.23ppm, DMSO-d_6(CD_3SOCD_3) 39.51ppm, ^{13}C : CD_3OH 49.2ppm) or a signal of the proton of the partly or non deuterated solvent (^{1}H : $CHCl_3$ in $CDCl_3$ δ7.24ppm, DMSO in DMSO-d_6 δ2.50ppm, ^{1}H : CH_3OH in CD_3OD -3.31ppm, 4.78ppm) with tetramethylsilane as internal reference. Chemical shifts (δ) are expressed in ppm. Structural elucidation was based on the interpretation of ^{1}H, ^{13}C, DEPT 90°, DEPT 135°, ^{1}H-^{1}H COSY, NOESY, ^{1}H-^{13}C direct correlation (HSQC) and ^{1}H-^{13}C long-range correlation (HMBC). Ultra violet (UV) spectra were recorded on Perkin Elmer Lambda 25 UV-Visible spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer Spectrum FT-IR spectrophotometer. Analytical thin layer chromatography (TLC) was carried out on silica gel Merck F_{254} precoated plates. Detection was made under ultraviolet light at wavelength 254nm and by spraying reagent (anisaldehyde − sulphuric acid)

followed by heating. Column chromatography (CC) was performed using silica gel 60H (Merck code TA1443034) as adsorbent/packing material. Gel filtration was done using sephadex LH-20 (Sigma-Aldrich). Preparative layer chromatography (PLC) was performed using Silica gel GF F_{254} (Analtech Uniplate Cat. Number 02012).

2.2 Plant Material

Fresh ripe fruits of *Napoleonaea imperialis* were harvested from Obinze in Owerri Capital Territory, Imo State, Nigeria. The plant was identified and authenticated by Mr. J. Opayemi, Department of Plant Science & Biotechnology, University of Port Harcourt and voucher sample, UPH 147, deposited at University of Port Harcourt Herbarium. The seeds were seperated from their rinds and were air-dried, and then crushed to coarse powder at room temperature and weighed.

2.3 Extraction

The dried powdered seeds (970g) were exhaustively extracted with n-butanol (1.5 liters) by cold maceration for 48 hours. The extracts were combined and concentrated to dryness using rotary evaporator to give a dark brown sticky crude extract (96.2g). The dark brown sticky crude extract (48g), was fractionated by solvent partitioning method using hexane, chloroform-distilled water (8:2) and n-butanol-water (8:2) to afford four extracts: hexane extract (9.7g) chloroform extract (23.9g), n-butanol extract (6.6g) and the aqueous extract (7.8g).

2.4 Isolation

The chloroform extract (5g) was chromatographed on a column (80 x 5cm) of silica gel (225g) and eluted successively with, hexane-EtOAc (6:4), 100% ethylacetate, and finally $CHCl_3$-MeOH-EtOAc-H_2O (15:22:40:10, lower phase). TLC was used to monitor the fractions and detection was carried out by spraying with anisaldehyde-H_2SO_4 spray reagent and heating. A total of 531 fractions of 20ml each were collected and combined on basis of TLC to afford 33 main fractions. The hexane-EtOAc (6:4) eluent (130mg) was purified on a column (45 x 1cm) of silica gel (3.9g) using hexane-EtOAc (8:2). A total of 203 fractions (1ml each) were collected, combined and analysed as follows:

Fractions 72-75 yielded a yellow solid compound **1** (2.8mg); R_f value 0.17 (hexane-EtOAc, 8:2; pink spot under UV light and purple spot with spray); mp 82-84 °C; uv (λ_{max}, nm) 325; ir (υ, cm^{-1}) 2959, 2800, 1735, 1460, 1260, 900, 800, 730; ^1H, ^{13}C-nmr (Table1).

Fractions 80-83 afforded a yellow solid compound 2 (6.4mg); R_f 0.15 (hexane-EtOAc, 8:2; a pink spot under the UV light and purple spot with spray); mp 79-81 °C, uv (λ_{max}, nm) 326, ir (υ cm^{-1}) 2918, 2849, 1737, 1673, 1521, 1217, 908, 732; ^1H, ^{13}C-nmr (Table 2).

Fractions 128-179 afforded a white solid compound 3 (8.7mg); R_f value 0.13 (hexane-EtOAc, 8:2; grayish-green spot with spray); mp 73-75 °C; ir (υ, cm^{-1}) 3039, 2938, 1737, 1612, 1500, 1368, 1216, 1026, 728; ^1H, ^{13}C-nmr (Table 3).

Elution of the column was continued with $CHCl_3$-MeOH-EtOAc-H_2O (15:22:40:10, lower phase) to get Fractions 474-485(120.2mg) and 494-504 (89.1mg) among other fractions.

Fractions 474-485 (120.2mg). On purification with activated charcoal and alumina, fractions (474-485) afforded compound 4 (37.5mg), a cream coloured powder. Compound 4 showed one purple spot, R_f 0.25 ($CHCl_3$-MeOH-H_2O, 65:35:10, lower phase); 0.05 ($CHCl_3$-MeOH-H_2O, 70:30:10, lower phase) and 0.4 (n-BuOH-AcOH-H_2O, 40:10:50, upper phase); mp 219-221 °C; ir (υ, cm^{-1}) 3320 (broad), 2970, 1239, 1034; ^1H, ^{13}C-nmr (Table 4).

Fractions 494-504 (89.1mg). The combined fractions (494 – 504) were packed on silica gel column (3g, 40 cm x 1.5 cm) and eluted with $CHCl_3$-MeOH-H_2O (70:20:10, lower phase) to obtain fractions 20-66 (43.4mg), which was further purified on preparative TLC silica gel and eluted with $CHCl_3$-MeOH-H_2O, 65:35:10, lower layer to afford a white Compound 5 (21.4mg). Compound 5 has Rf 0.21 (not visible in UV but green colouration with spray); ir (υ, cm^{-1}), 3300 (broad), 2940 and 1030; ^1H, ^{13}C-nmr (Table 5).

3. Results and Discussion

The crushed powdered seeds of *N. imperialis* were extracted with n-butanol and the extract was partitioned into hexane, chloroform, n-butanol and aqueous fractions. The chloroform extract was chromatographed using various solvents to obtain compounds 1-5.

Compound 1, mp 82-84 °C, had IR absorptions (Fig. 1) at 1735, 1260 1215 cm^{-1}(ester), 1610 cm^{-1} (C=C). ^1H-nmr (Table 1, δ) had 9.64(s, H-1), 7.66(m, H-2), 7.43(m, H-4), 6.45(H-3), 4.7(s, H-16). The ^{13}C NMR spectrum (Table 1 δ) showed 16 carbons while its DEPT spectrum revealed the presence of three carbon singlets at 177.5 (C-15, carbonyl carbon), 167.7 and 132.4 (C-10 and

Table 1: NMR (^{13}CNMR 100.63 MHz and ^1HNMR 400.22 MHz in $CDCl_3$) data for Compound 1

Position	δ ^{13}C	δ ^1H
1	30.3(d)	9.64(s)
2	130.8(d)	7.66(m)
3	109.9(d)	6.45
4	128.8(d)	7.43(m)
5	132.4(s)	-
6	14.0(t)	0.78
7	10.9(t)	0.80(m)
8	29.6(d)	1.26(m)
9	28.9(d)	1.30
10	167.7(s)	-
11	68.1(d)	4.13(m)
12	38.7(t)	1.65(m)
13	23.7(t)	1.38(m)
14	22.9(t)	1.25(m)
15	177.5(s)	-
16	57.7(q)	4.70(s)

C-5, two aromatic carbons), seven doublets at 130.8(C-2), 128.8(C-4), 109.9(C-3), 68.1(C-11), 30.3(C-1), 29.6(C-8), and 28.9(C-9), five tertiary carbons at 38.7(C-12), 23.7(C-13), 22.9(C-14), 14.0(C-6), 10.9(C-7) and one quartenary carbon at 57.7(C-16). The HSQC spectrum (Fig. 2) was used to assign protons to the individual carbons.

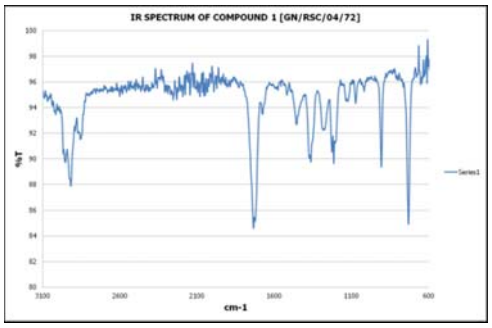


Fig 1: ftir spectrum of compound 1

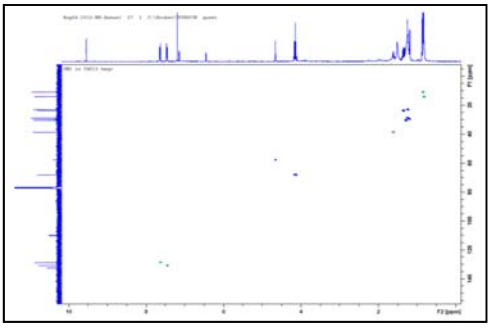


Fig 2: $^{1}H - {}^{13}C$ hsqc nmr spectrum of compound 1

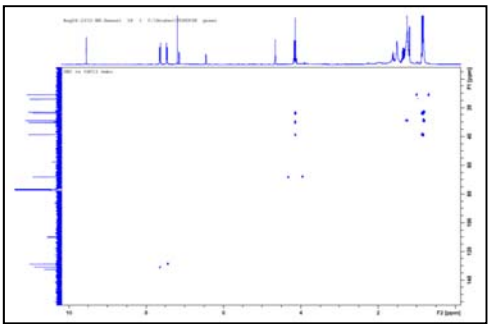


Fig 3: $^{1}H - {}^{13}C$ hmbc nmr spectrum of compound 1

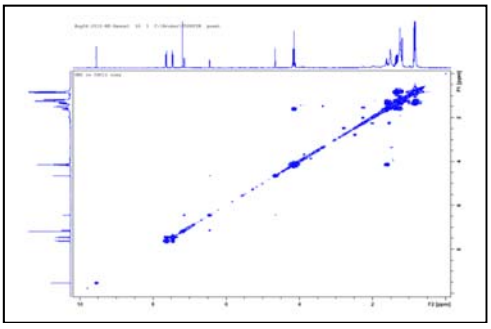


Fig 4: $^{1}H - {}^{1}H$ cosy nmr spectrum of compound 1

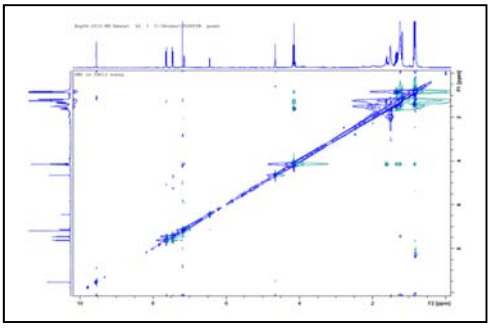
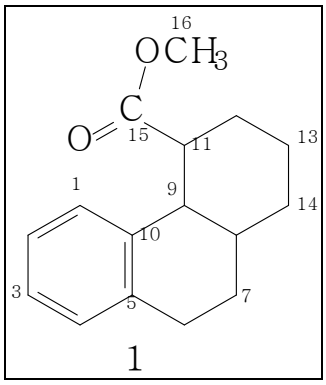


Fig 5: $^{1}H - {}^{1}H$ noesy nmr spectrum of compound 1

The complete assignment of compound 1 was accomplished using HMBC (Fig. 3), COSY (Fig. 4) and NOESY (Fig. 5) spectra. In comparison with published data of related compounds [14, 15], compound 1 was characterized as methyl-1,3,5-triene-tricyclopentadecanoate (1).



1

Compound **2** was isolated as a yellow solid. Its IR spectrum showed absorption at 1737, 1217 cm^{-1} (carbonyl of lactone), 1610, 1521, 908 and 732cm^{-1} (aromatic substitution). The ^{1}H-nmr

Table 2: NMR (^{13}CNMR 100.63 MHz and ^{1}HNMR 400.22 MHz in $CDCl_3$) data for Compound 2

Position	δ ^{13}C	δ ^{1}H
2	177.6(s)	-
3	29.6(t)	1.23, 9.58
4	31.9(t)	1.23(s)
5	29.3(s)	-
6	57.7(t)	4.70(s)
7	152.4(s)	-
8	109.9(d)	6.50(d)
9	122.5(d)	7.24(d)
10	160.3(s)	-
11	122.5(d)	7.24(d)
12	109.9(d)	6.50(d)
13	14.1(q)	0.83
14	22.6(q)	0.79

spectrum (Table 2, δ) had four doublets at 7.24 (2H, H-9 and H-11), 6.50 (2H, H-8 and H-12), one singlet at 4.70 (H-6). ^{13}C-nmr (Table 2, δ) and its DEPT spectra revealed the presence of four singlets at 177.6 (C-2, carbonyl of lactone), 160.3 (C-10, tetrasubstituted C=C), 152.4 (C-7, tetrasubstituted C=C), 29.3 (C-5, tetrasubstituted carbon), four doublets at 109.9 (C-8), 122.5 (C-9 and C-11), 109.9 (C-12), three triplets at 29.6 (C-3), 31.9 (C-4), 57.7 (C-6), two quartets at 14.1 (C-13) and 22.6 (C-14). Protons were assigned to individual carbons based on the HSQC (Fig. 6) while positions of the carbons were based on the HMBC (Fig. 7), COSY (Fig. 8) and NOESY (Fig. 9) spectra interpretation.

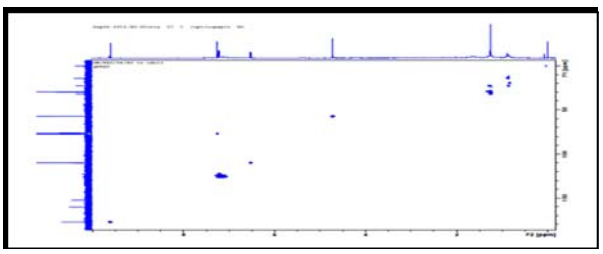


Fig 6: $^{1}H - {}^{13}C$ hsqc nmr spectrum of compound 2

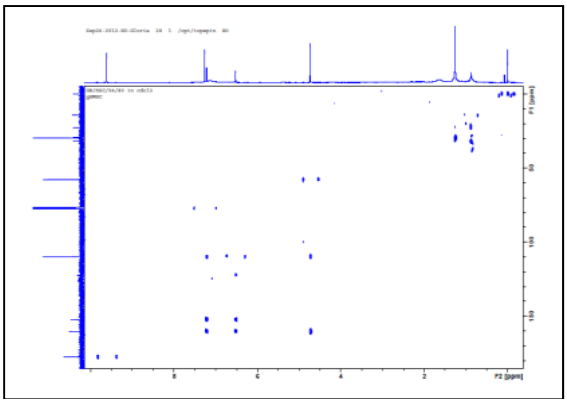


Fig 7: $^{1}H - ^{13}C$ hmbc nmr spectrum of compound 2

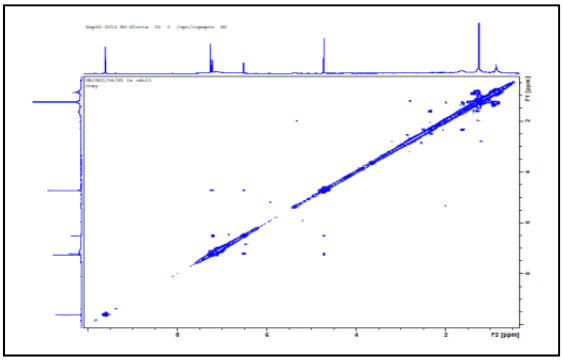


Fig 8: $^{1}H - ^{1}H$ cosy nmr spectrum of compound 2

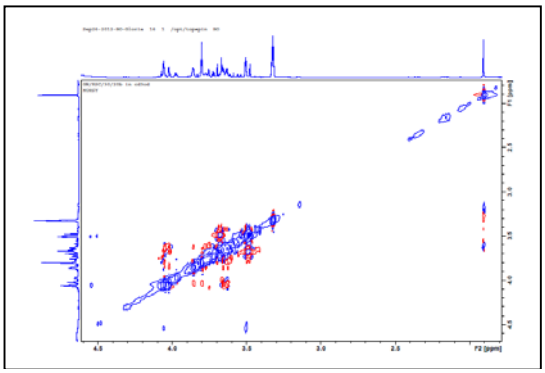
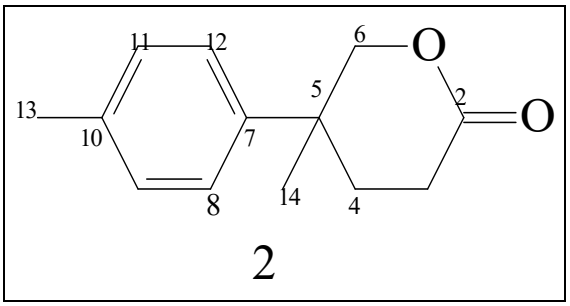


Fig 9: $^{1}H - ^{1}H$ noesy nmr spectrum of compound 2

Compound 2 (napoleonapyran-2-one, 2) was characterized as 5-methyl-5-toluyl-3,4,6-trihydropyran-2-one.



2

Compound 3, a white solid, exhibited IR absorption bands at 1737cm^{-1}(ester), 3039, 1612, 1500, and 728cm^{-1} (aromatic monosubstitution), 1216, 1099 and 1026cm^{-1} (ether linkage). The ^{1}H-NMR (Table 3, δ) showed signals at 3.66 (dd, H-4), 3.81 (m, H-8) and 4.19 (m, H-18), respectively.

Table 3: NMR ($^{13}CNMR$ 100.63 MHz and $^{1}HNMR$ 400.22 MHz in $CDCl_3$) data for Compound 3

Position	δ ^{13}C	δ ^{1}H
1	22.6(t)	1.34
2	24.9(t)	1.60(s, broad)
3	31.9(t)	1.28(d)
4	63.3(d)	3.66(dd)
5	34.1(d)	2.34
6	25.6(t)	1.2(d), 2.74(m)
7	31.5(t)	1.23
8	70.2(d)	3.81(m)
9	27.2(t)	2.06(m)
10	29.7(d)	1.20
11	174.3(s)	-
12	128.0(d)	5.33(m)
13	130.2(d)	5.31(m)
14	129.7(d)	5.35(m)
15	127.8(d)	5.32(m)
16	129.7(d)	5.35(m)
17	130.2(d)	5.31(m)
18	65.1(t)	4.19(m)
19	14.1(q)	1.25

The ^{13}C-NMR (Table 3, δ) and its DEPT spectra showed the following signals: 14.1(q, C-19), 22.6(t, C-1), 24.9(t, C-2), 25.6(t, C-6), 27.2(t, C-9), 29.7(d, C-10), 31.5(t, C-7), 31.9(t, C-3), 34.1(d, C-5), 63.3(d, C-4), 65.1(t, C-18), 70.2(d, C-8), 127.8(d, C-15), 128.0(d, C-12), 129.7(d, C-14, C-16), 130.2(d, C-13, C-17) and 174.3(s, C-11). Protons were assigned to their respective carbons using the HSQC (Fig. 10), while the HMBC (Fig. 11), COSY (Fig. 12) and NOESY (Fig. 13) spectra analysis were the basis for the carbon positions. H-4 showed an HMBC correlation with C-18, and H-18 showed HMBC correlations with C-4 and C-19. The result suggested that C-4 was linked to C-18 by an ether linkage [14]. Compound 3 was characterized as 4-ethoxy-bicyclodecylbenzoate (3).

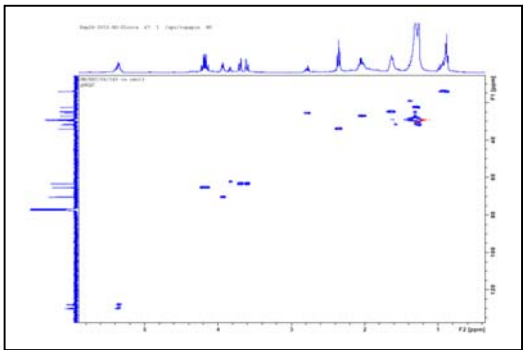


Fig 10: $^{1}H - ^{13}C$ hsqc nmr spectrum of compound 3

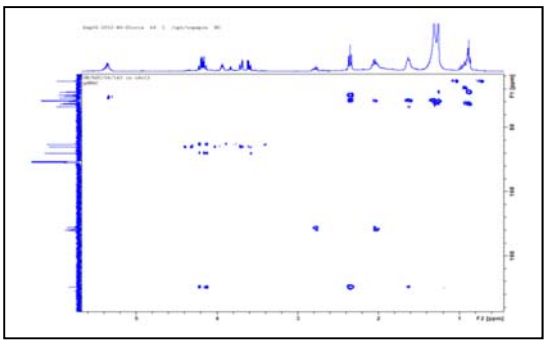


Fig 11: $^{1}H - ^{13}C$ hmbc nmr spectrum of compound 3

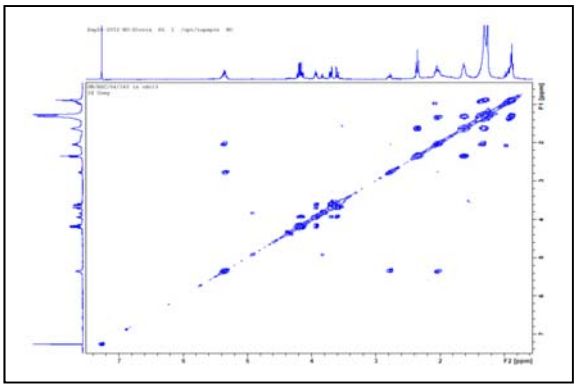


Fig 12: $^{1}H - {}^{1}H$ cosy nmr spectrum of compound 3

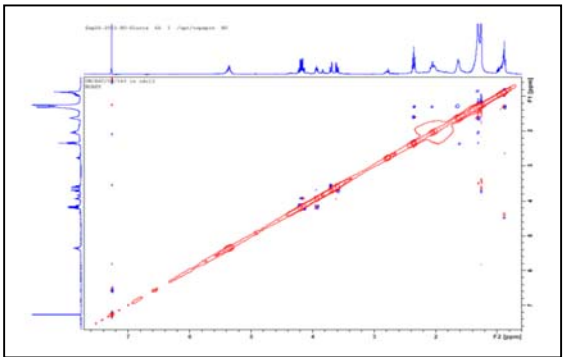
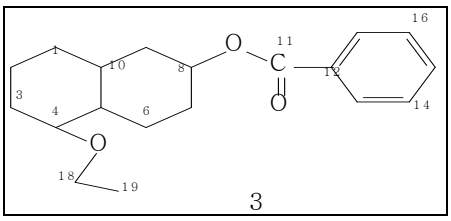


Fig 13: $^{1}H - {}^{1}H$ noesy nmr spectrum of compound 3



Compound 4 was isolated as a cream-coloured powder. The IR spectrum exhibited two broad absorption bands at 3320 and 1034 cm^{-1} for hydroxyl (suggesting the existence of a glycosidic structure [16,17]); 1700cm^{-1} for carbonyl and 1600cm^{-1} for trisubstituted olefin. The ^{1}H-NMR spectrum (Table 4, δ) showed signals characteristic of seven tertiary methyl groups as singlets at 0.82, 0.92, 0.95, 1.14, 1.20, 1.25 and 2.07. Three anomeric protons at 4.57, 4.55 and 4.51 were, respectively, correlated to three anomeric carbons at 104.5, 104.4 and 103.4 in HSQC spectrum (Fig. 14); indicating the presence of three monosaccharides which were determined to be three β-D-glucopyranoses The assignments of the protons and carbons were established as listed in Table 4 [18, 19,12].

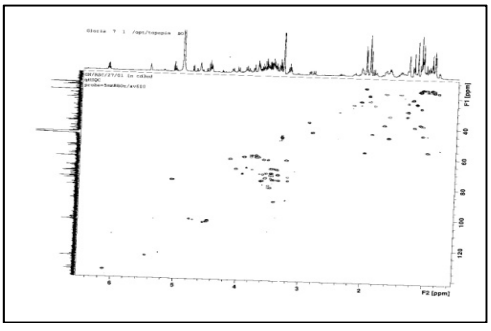


Fig 14: $^{1}H - {}^{13}C$ hsqc nmr spectrum of compound 4

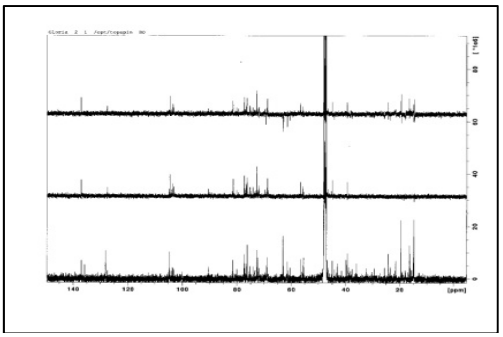


Fig 15: ^{13}C dept nmr spectrum of compound 4

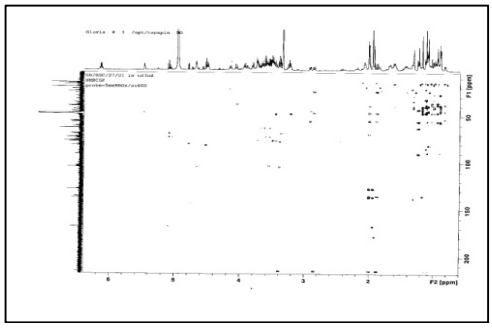


Fig 16: $^{1}H - {}^{13}C$ hmbc nmr spectrum of compound 4

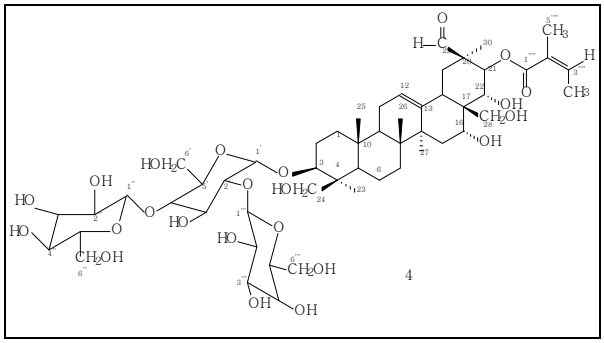
Table 4: NMR (^{13}CNMR 150.89 MHz and ^{1}HNMR 600.1 MHz in CD_3OD) data for Compound 4

Aglycon			Sugar moiety		
Position	**δ ^{13}C**	**δ ^{1}H**	**Position**	**δ ^{13}C**	**δ ^{1}H**
1	38.9(t)	1.00, 1.70	1′	104.5(d)	4.57(d)
2	25.5(t)	1.25, 1.40	2′	74.1(d)	3.60
3	90.5(d)	3.43(m)	3′	76.2(d)	3.39
4	44.9(s)	-	4′	80.0(d)	3.54
5	56.5(d)	0.99(m)	5′	75.2(d)	3.56
6	19.3(t)	2.01, 2.01	6′	61.2(t)	3.93
7	32.4(t)	1.24, 1.68	1″	104.4(d)	4.55
8	39.8(s)	-	2″	72.7(d)	3.50
9	46.8(d)	2.86	3″	75.3(d)	3.21
10	35.9(s)	-	4″	71.9(d)	3.92
11	24.2(t)	1.94, 2.18	5″	76.5(d)	3.63
12	126.8(d)	5.44(s)	6″	62.8(t)	3.75
13	136.0(s)	-	1‴	103.4(d)	4.51
14	43.0(s)	-	2‴	72.6(d)	3.89
15	37.5(t)	1.05, 1.18	3‴	77.4(d)	3.51
16	68.8(d)	3.86	4‴	69.4(d)	3.22
17	48.1(s)	-	5‴	77.1(d)	3.61
18	39.4(d)	2.90(d)	6‴	63.0(t)	3.66
19	47.8(t)	1.62, 3.27			
20	46.4(s)	-			
21	76.6(d)	5.10			
22	72.4(d)	3.91(d)			
23	23.4(q)	2.07(s)			
24	60.4(t)	3.87(d);3.25			
25	16.1(q)	0.82(s)			
26	16.3(q)	0.95(s)			
27	29.3(q)	1.20(s)			
28	61.4(t)	3.94(d);3.25			
29	215.4(d)	8.56(s)			
30	14.8(q)	0.92			
1””	168.0(s)	-			
2””	128.1(s)	-			
3””	135.7(d)	6.13(q)			
4””	16.0(q)	1.14			
5””	21.4(q)	1.23			

The ^{13}CNMR spectrum of compound 4 (Table 4, δ) analyzed with the aid of DEPT (Fig. 15) and ^{1}H – detected HSQC (Fig. 14) revealed the presence of 53 carbon atoms in the molecule. DEPT was used for the determination of carbon multiplicities in the ^{13}C-NMR. The presence of a trisubstituted olefinic linkage at Δ^{12} was confirmed by the ^{1}H-NMR signal at 5.44(br s) [20] and ^{13}C-NMR signals at 126.8(d), 136.0(s) [21, 22].

From the above data and by comparing the ^{13}CNMR data of compound 4 with literature reports for triterpenoids, the aglycon was identified as olean-12-ene-3,16,21,22,24,28-hexahydroxy-29-al [21,23]. Five carbon signals [an ester carbonyl δ168.0 (C-1""), a quaternary olefinic carbon 128.1 (C-2""), an olefinic methine 135.7 (C-3""), methyl signals at 16.0 (C-4"") and 21.4 (C-5"") corresponded to an angeloyl group [12]. HMBC spectrum (Fig. 16) of compound 4 showed the correlation peak between H-21 (5.10) and the carbonyl carbon (168.0) of the angeloyl group. Thus the linkage site of the angeloyl group must be at C-21 [16, 17].

There were eighteen carbon signals (Table 4, δ) for the sugar moiety including three anomeric carbons at 104.5, 104.4 and 103.4 from which the presence of three glucose units was indicated. The downfield shift of an oxygen-bearing methine C-3 (δ90.5), indicated the site of glycosylation [21, 24]. The above proposed inter-glycosidic linkage was substantiated by the long-range correlation observed in the ^{1}H – detected HMBC spectrum (Fig. 16) of compound 4. Cross peaks between H-1′/C-1′ (4.57/104.5) of one glucose unit and H-3/C-3 (3.43/90.5) of the aglycone showed the sugar moiety to be attached to C-3 of the aglycone. The spectra data of compound 4 corresponded to that reported [16, 17] but differed in the absence of a glucoronic acid (from the sugar moiety) and presence of an aldehydic carbon at position 29 [21, 29]. On the basis of the above evidence, structure 4, Napoleon aside-B, is characterized as 3β-O-[β-D-glucopyranosyl(1→2)][β-D-glucopyranosyl(1→4)][β-D-glucopyranosyl]-16α,22α,24,28-tetrahydroxy-21-β-O-angeloxyolean-12-ene-29-al.



Compound 5 was isolated as white powder from $CHCl_3$-MeOH-H_2O (65:35:10, lower phase). Its IR spectrum showed absorptions at 3300 cm^{-1} (broad, H-bonded hydroxy group) and 1020cm^{-1} (ether), which indicated the presence of a glycosidic structure. The ^{1}HNMR (Table 5, CD_3OD, δ) exhibited signals between 3.31 − 4.09, typical of a glycoside [18, 19], 1.35(s, 3H, H-12), 1.90(s, 3H, H-11) and an anomeric proton signal at 4.02. The ^{13}C NMR (Table 5, δ) revealed the presence of four carbon bearing OH groups at 77.9(d, C-2), 99.2(s, C-4), 84.2(s, C-5), 105.8(s, C-10) on the aglycone [15] and one anomeric carbon at 103.1(C-1'). The NMR signals (Table 5, CD_3OD, δ) of the sugar moiety suggested it to be β-D-glucopyranosyl [18]. The attachment of the glucose group at C-3 was deduced from ^{1}H – detected HMBC (Fig. 17), which showed long-range correlation in which H-1' (4.02) and H-3 (3.82) were correlated with C-3 (69.3), and C-1' (103.1). As a result of the analysis of its HMBC (Fig. 17), DEPT (Fig. 18), HSQC (Fig. 19), COSY (Fig. 20) and NOESY (Fig. 21), the structure of compound 5 was characterized as 3-O-[β-D-glucopyranosyl]-1,4-dimethyl-2,4,5,10-tetrahydroxy-bicyclodecane (5).

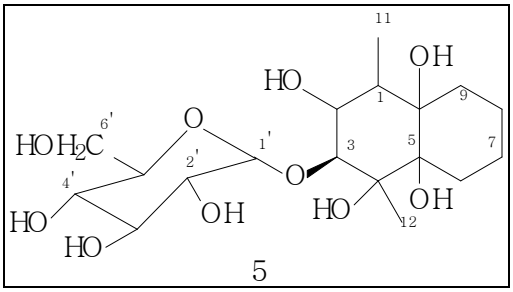


Table 5: NMR (^{13}CNMR 100.63 MHz and ^{1}HNMR 400.22 MHz in CD_3OD) data for Compound 5

Position	δ ^{13}C	δ ^{1}H
1	71.8(d)	3.85(s)
2	77.9(d)	3.96(d)
3	69.3(d)	3.82
4	99.2(s)	-
5	84.2(s)	-
6	62.6(t)	3.76
7	64.1(t)	3.72
8	64.5(t)	3.69, 3.47
9	65.1(t)	3.68, 3.44
10	105.8(s)	-
11	24.2(q)	1.90(s)
12	30.7(q)	1.35(s)
1’	103.1(d)	4.02(s)
2’	77.5(d)	4.05
3’	76.7(d)	4.07
4’	83.2(d)	3.75(s)
5’	71.2(d)	3.80
6’	65.8(t)	3.50, 3.71

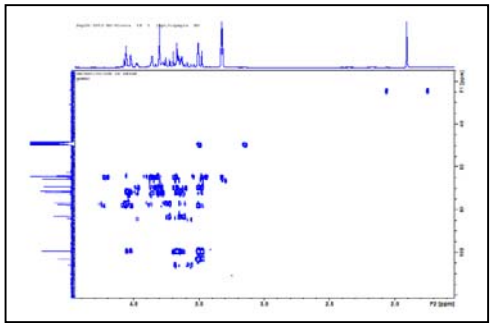


Fig 17: ^{1}H – ^{13}C hmbc nmr spectrum of compound 5

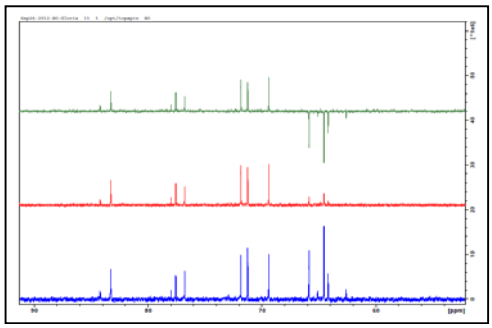


Fig 18: ^{13}C dept nmr spectrum of compound 5

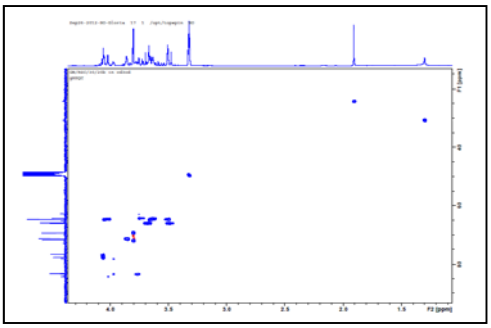


Fig 19: $^{1}H - ^{13}C$ hsqc nmr spectrum of compound 5

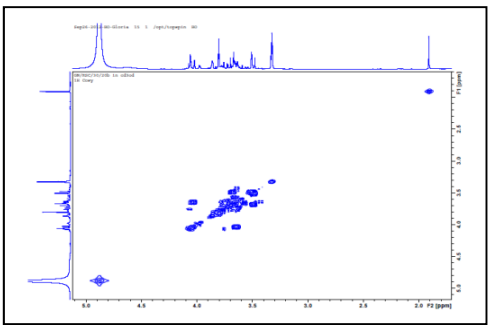


Fig 20: $^{1}H - ^{1}H$ cosy nmr spectrum of compound 5

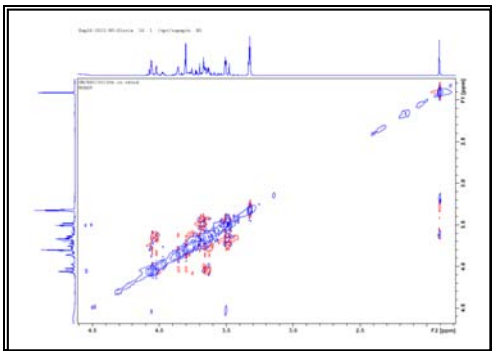


Fig 21: $^{1}H - ^{1}H$ noesy nmr spectrum of compound 5

4. Conclusion

This work reports the successful isolation of five novel compounds from the fruit of *Napoleonaea imperialis*. The compounds were characterized as methyl-1,3,5-triene-tricyclopentadecanoate (1); 5-methyl-5-toluyl-3,4,6-trihydropyran-2-one (2, napoleonapyran-2-one); 4-ethoxy-bicyclodecylbenzoate(3); 3β-O-[β-D-glucopyranosyl (1→2)][β-D-glucopyranosyl(1→4)][β-D-glucopyranosyl]-16α,22α,24,28-tetrahydroxy-21-β-O-angeloxyolean-12-ene-29-al (4, napoleon aside-B) and 3-O-[β-D-glucopyranosyl]-1,4–dimethyl-2,4,5,10-tetrahydroxy–bicyclodecane (5).

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6. References

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