^{13}C NMR ANALYSIS: TERPENOIDS, STEROIDS AND CAROTENOID FROM *DIOSPYROS SOUBREANA* (EBENACEAE)

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ABSTRACT

Phytochemical investigations on bark of trunks and leaves of *Diospyros soubreana* (Ebenaceae) led to the isolation and characterization of nine molecules: one monocyclic sesquiterpenoid lactone (**1**), five pentacyclic triterpenes (**2**, **3**, **4**, **5** and **6**), two sterols (**7** and **8**) and one carotenoid alcohol (**9**), all isolated for the first time from this species. The structural elucidation of these compounds was carried out by ^{13}C NMR spectroscopy.

Keywords: *Diospyros soubreana*, terpenoids, steroids, carotenoid, ^{13}C NMR spectroscopy.

1. INTRODUCTION

In the last decades, many studies on *Diopyros* species have been conducted due to their medicinal and their economic importance. These studies focused on the chemical composition and biological activities of extracts and secondary metabolites. Chemical investigations have shown that *Diopyros* contained various bioactive compounds such as triterpenoids, naphtoquinones, naphthalene derivatives, flavonoids and coumarin derivatives [1].

Diospyros soubreana F. White (also called *Maba soubreana* A. Chev.) belonging to the family Ebenaceae, is a tropical tree found in West Africa from Ivory Coast to South Nigeria. To the best of our knowledge, very few pharmacological and chemical data exist on this species. Moreover, the leaves of this plant are used as wound healing in Ivory Coast [2, 3].

We earlier reported the isolation of three isocoumarins namely bergenin, norbergenin and 4-*O*-galloylnorbergenin, along with a new naphthalene derivative from the leaves and the bark of trunks of this plant [1, 4]. In continuation of the research on the chemical constituents of this species, our investigation reports for the first time some secondary metabolites which previously showed biological activities in the treatment of numerous human diseases. To the best of our knowledge, this is the first report on the isolation of these compounds from *D. soubreana*. These compounds were identified by ^{13}C NMR spectroscopy which is a valuable tool for phytochemicals identification.

2. MATERIALS AND METHODS

2.1. General

The ^{13}C NMR spectra were recorded on a Bruker Avance 400 Fourier Transform spectrometer operating at 400 MHz for ^{1}H spectra and 100 MHz for ^{13}C using CD_3OD and Me_2CO-d_6 as deuterated solvents. The chemical shift was expressed in ppm from TMS (internal standard). The chromatography columns were performed on silica gel (Merck, 35-70 µm, 60-200 µm and 63-200 µm). Thin-layer chromatographies were carried out on aluminium plates coated with silica gel 60-F_{254} (Merck), and visualized with UV light (254 and 366 nm), then sprayed with vanillin-H_2SO_4 solution followed by warming.

2.2. Plant material

Leaves and bark of trunks of *D. soubreana* were collected in July 2014 in « Petit Yapo » forest, Agboville Department (5°55'59.999''N, 4°13'0.001''W), south-east of Côte d'Ivoire. The plant samples were identified by a botanist of Centre National de Floristique (CNF), University Félix Houphouët-Boigny of Cocody-Abidjan, where a voucher specimen is deposited under the reference DS-BOUE-Agboville 2014-1. The samples were dried at room temperature, then ground. 100 g of leaf powder (DSF) and 120 g of trunk bark powder (DST) were obtained.

2.3. Extraction and isolation

100 g of leaves powder (DSF) were extracted by maceration three times with 500 mL of the mixture water/ethanol (70 : 30) for 24 h at room temperature (25°C). After filtration and the removal of the solvent under reduced pressure, a residue of 25.5 g was obtained. 15 g of this residue was suspended in ethanol 70% (100 mL) and extracted sequentially with increasing polarity solvents to give after evaporation 0.88 g of *n*-hexane (DSFH), 1.82 g of dichloromethane (DSFD) and 2.39 g of ethyl acetate (DSFA) extracts.

Powdered bark of trunks (120 g) were extracted in a Soxhlet apparatus, firstly with petroleum ether (500 mL) and then with dichloromethane (500 mL), followed by maceration in 600 mL of ethyl acetate at room temperature (25°C). Extracts were filtered and concentrated under reduced pressure to give 0.8 g of petroleum ether (DSTPE), 1.2 g of dichloromethane (DSTD) and 9.7 g of ethyl acetate (DSTA) extracts. 388 mg of the leaves dichloromethane extract (DSFD) was chromatographed on a silica gel column (63-200 µm) using a gradient of hexane/ethyl acetate (100 : 0 to 0 : 100) to give twelve fractions (FD1-FD12) along with 15-

pentadecanolide (**1**) (89.7 mg) [5]. Fraction FD5 (54.8 mg) was constituted by the mixture α-amyrin (**2**), β-amyrin (**3**) [6] and lupeol acetate (**5**) [7]. Fraction FD6 (40 mg) was successively purified by silica gel chromatography (63-200 µm), first with the gradient hexane/ethyl acetate (100 : 0 to 70 : 30) and then hexane/ethyl acetate (80 : 20) to furnish four fractions (FD61-FD64) according to their TLC profiles. Fraction FD62 (5.7 mg) was the mixture α-amyrin (**2**), β-amyrin (**3**) and lupeol (**4**) [6], while fraction FD63 (4.3 mg) was the mixture stigmasterol (**7**) and β-sitosterol (**8**) [8].

A part of the extract DSFA (2 g) was subjected to a vacuum chromatography using a gradient of petroleum ether/ethyl acetate (100 : 0 to 0 : 100) then ethyl acetate/methanol (80:20) to provide six major fractions (FA1-FA6). The fraction FA4 (112.9 mg), treated by successive chromatographies on silica gel columns (35-70 µm and 60-200 µm) eluted with the gradient dichloromethane/ethyl acetate (100 : 0 to 40 : 60), then with dichloromethane/ethyl acetate (50 : 50) led to 7.1 mg of zeaxanthin (**9**) [9].

The extract DSTD (1.2 g) was chromatographed on a silica gel (63-200 µm) column (hexane/EtOAc, 100 : 0 to 0 : 100, then EtOAc/MeOH 90 : 10) to provide 35.7 mg of betulinic acid (**6**) [6].

3. RESULTS AND DISCUSSION

From the leaves and bark of trunks of *D. soubreana*, nine compounds were isolated and identified. The structures of these compounds (Fig. 1) were established by the main of ^{13}C NMR analysis and by comparison with literature data. Spectral data for the compounds (**1**-**9**) are proposed as **supporting information**. These molecules corresponded to one monocyclic sesquiterpenoid lactone (**1**), five pentacyclic triterpenoids (**2**, **3**, **4**, **5** and **6**), two ubiquitous sterols (**7** and **8**) and one carotenoid alcohol (**9**), all isolated for the first time from this plant.

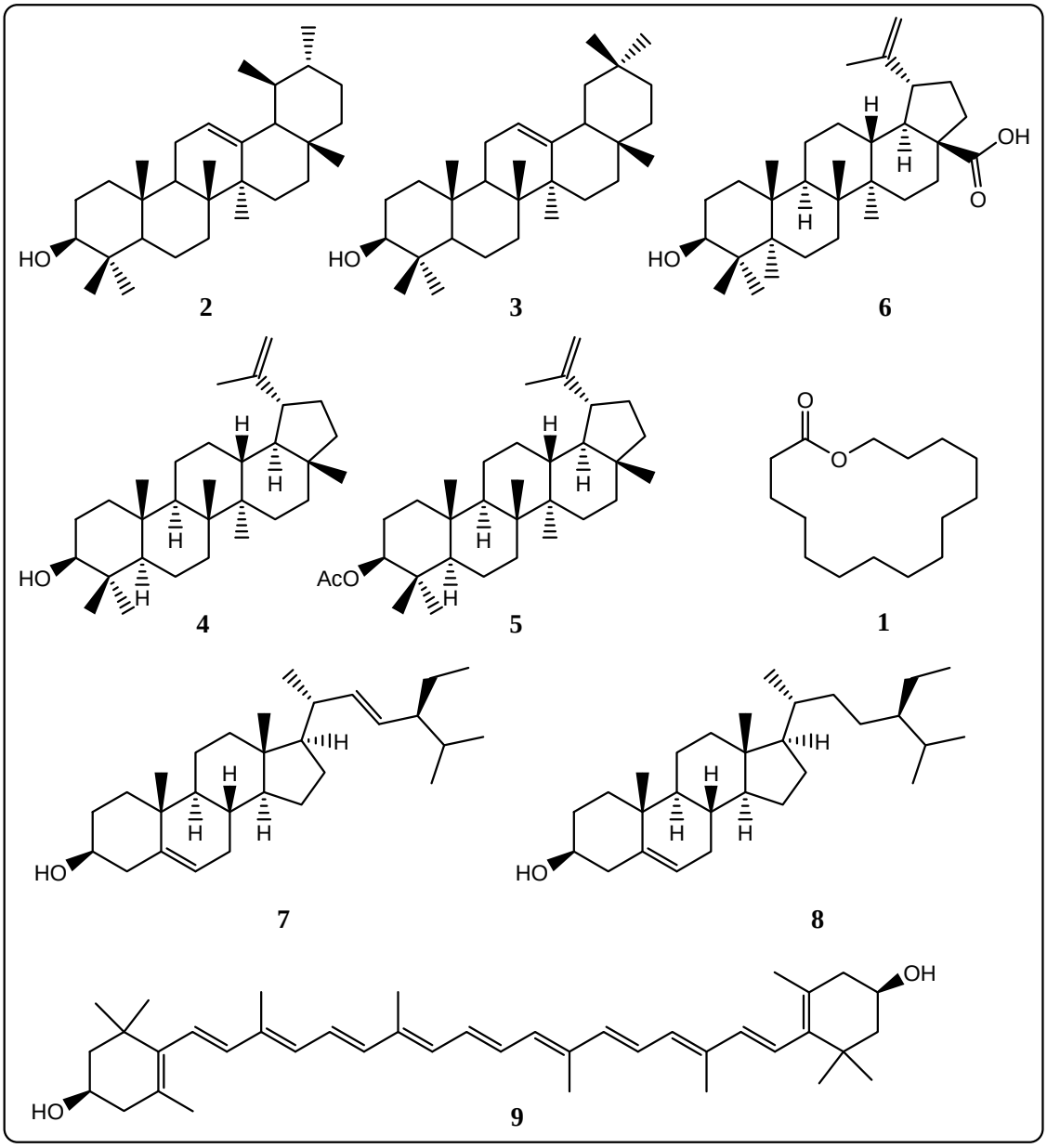

Fig. 1: Structures of isolated compounds from *diospyros soubreana*

Pentacyclic triterpenoids [10, 11] and phytosteroids [12] are class of compounds occurring widely in plants. Biosynthetically, these compounds have squalene as precursor [13]. Phytosterols are a family of more than 200 different compounds [12]; the richest source of phytosterols is composed of plant based foods stuff chiefly nuts, seeds, vegetable oils, cereals and legumes [14-16]. Pentacyclic triterpenes and steroids, which are present in all plant organs, are usually isolated from apolar and medium polar extracts. In this study, these compounds, which constitute the bulk of the isolated molecules, were isolated from the leaf

(DSFD) and trunk bark (DSTD) dichloromethane extracts (see experimental part). Otherwise, only zeaxanthin (**9**) was derived from a polar extract (ethyl acetate extract of the leaves). Indeed, this compound is generally isolated from polar extracts. Zeaxanthin which is one of the most common carotenoid alcohols found in nature, is a xanthophyll from higher plants, algae [17] and microbial sources [18]. It is the main pigment of yellow corn, *Zeaxanthin mays* L. (from which its name is derived). Zeaxanthin is naturally found in various dietary sources including corn, egg yolk, orange pepper, orange juice, honeydew, mango, avocado, and other vegetables and fruits.

Although no biological activity tests were conducted on the isolated compounds (**1**-**9**), literature search revealed that these have diverse bioactivities (Table 1).

Table 1: Biological activities of isolated compounds

Compounds	Biological activities	References
15-pentadecanolide (**1**)	minimal irritancy, allergenicity and acute toxicity	[19]
α-amyrin (**2**)	anti-inflammatory, anti-microbial, anti-ulcer, anti-hyperlipidemic, anti-tumor, hepatoprotective	[20], [21], [22]
β-amyrin (**3**)	anti-inflammatory, anti-microbial, antibacterial, antinociceptive, antioxidant activities, liver protection	[11], [20], [21], [22], [23], [24], [25]
Lupeol (**4**)	antiprotozoal, anti-inflammatory, antimicrobial, antitumor, cancer chemopreventive, cardioprotective, gastroprotective, hepatoprotective effects	[26]
Lupeol acetate (**5**)	hypotensive, antimicrobial, anti-inflammatory, antimalarial, antituberculosis, antinociceptive, antiarthritic, antifertility	[27], [28], [29], [30], [31]
Betulinic acid (**6**)	antibacterial, antinociceptive, antioxidant, anti-inflammatory, anthelmintic, antimalarial, antitumor, anti-HIV	[32], [33], [34], [35]
Stigmasterol (**7**)	antioxidant, anti-inflammatory, anti-osteoarthritic, antimutagenic, anti-hypercholestrolemic, hypoglycemic, thyroid	[36]

	inhibiting, cytotoxic, antitumor	
β-sitosterol (**8**)	anti-inflammatory, antioxidant, hypocholesterolemic, analgesic, anthelminthic, anti-mutagenic, immunomodulatory, neuroprotection, antidiabetic, reduced the growth and spread of prostate cancer cells, induced apoptosis, chemoprotective, angiogenic, antibacterial, antifungal, mosquito larvicidal	[37], [38], [39]
Zeaxanthin (**9**)	prevention of age-related macular degeneration, cancer-preventive, inhibits macrophage-mediated LDL oxidation	[40], [41]

In sum, the presence of terpenes and steroids in the leaves of the plant could justify the use of this part of the plant as wound healing.

4. CONCLUSION

This study conducted on the leaves and stem barks of *D. soubreana* led to the isolation and identification of nine compounds, all isolated for the first time from this species. Their structures have been established using ^{13}C NMR spectroscopy. These molecules belong to various chemical groups including terpenoids, steroids and carotenoids. The literature review carried out on them made it possible to demonstrate multiple biological activities.

The presence of anti-inflammatory compounds such as lupeol, lupeol acetate, α-amyrin, β-amyrin, β-sitosterol and stigmasterol in the leaves may justify the use of this part of the plant to treat wounds. In addition, this plant could be a potentially source of antioxidant compounds. This study is worth pursuing in order to isolate other bioactive compounds. Moreover, biological tests deserve to be done to highlight other pharmacological potentialities.

Ethical Approval:

As per international standard or university standard ethical approval has been collected and preserved by the authors.

ACKNOWLEDGEMENT

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CONFLICT OF INTEREST

We declare no conflict of interest for this research.

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List of Supplementary Material

Table S1. ^{13}C (125 MHz) NMR data of compound **1**

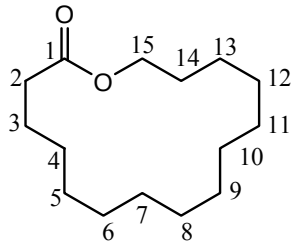
Table S2. ^{13}C (125 MHz) NMR data of compounds **2**, **3** and **4**

Table S3. ^{13}C (125 MHz) NMR data of compound **5**

Table S4. ^{13}C (125 MHz) NMR data of compound **6**

Table S5. ^{13}C (125 MHz) NMR data of compounds **7** and **8**

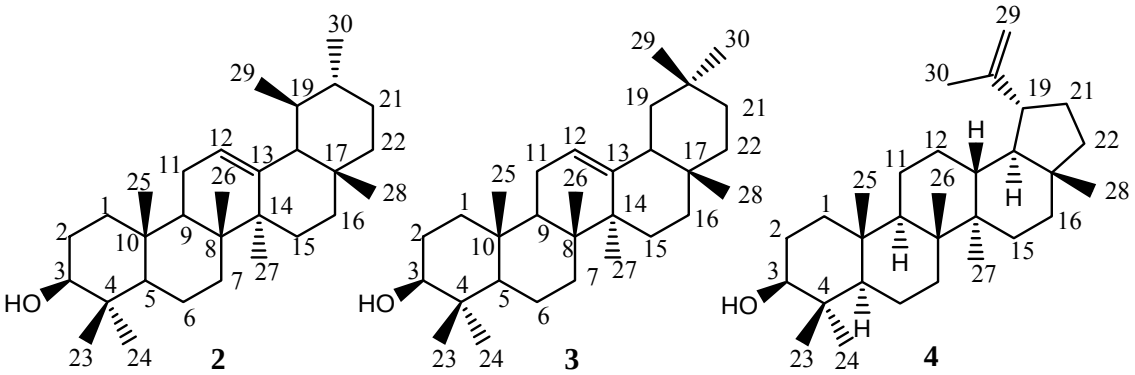
Table S1. ^{13}C (125 MHz) NMR data of compound **1**



N°C	δ ^{13}C (ppm)	δ ^{13}C (*) (ppm)
1	171.8	173.7
2	34.2	34.4
3	25.1	25.2
4	26.1	26.1
5	26.6	26.4
6	28.4	28.5
7	27.1	27.2
8	27.1	27.2
9	27.1	27.2
10	27.0	27.0
11	27.8	27.8
12	26.9	26.7
13	25.0	24.9
14	25.9	25.9
15	64.4	63.8

(*) Trost and Verhoeven, 1980

Table S2. ^{13}C (125 MHz) NMR data of compounds **2**, **3** and **4**

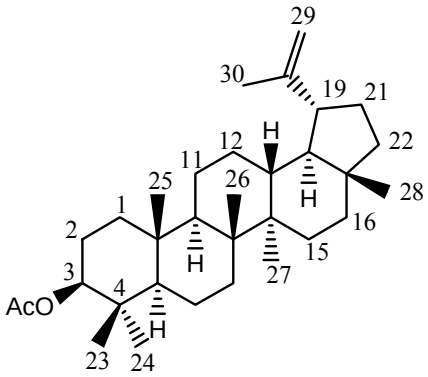


	2		**3**		**4**	
N°C	δ ^{13}C (ppm)	δ ^{13}C (*) (ppm)	δ ^{13}C (ppm)	δ ^{13}C (*) (ppm)	δ ^{13}C (ppm)	δ ^{13}C (*) (ppm)
1	38.7	38.7	38.7	38.7	38.7	38.7
2	27.2	27.2	27.2	27.3	27.4	27.4
3	79.0	78.3	79.0	79.0	79.0	78.9
4	38.7	38.7	38.8	38.8	38.7	38.8
5	55.1	55.2	55.2	55.3	55.2	55.3
6	18.3	18.3	18.3	18.5	18.3	18.3
7	31.9	32.9	32.6	32.8	34.2	34.2
8	40.0	40.0	38.8	38.8	40.8	40.8
9	47.7	47.7	47.7	47.7	50.4	50.4
10	36.8	36.9	38.0	37.6	37.1	37.1
11	23.2	23.3	23.5	23.6	20.9	20.9
12	124.4	124.3	121.7	121.8	25.1	25.1
13	139.5	139.3	145.1	145.1	38.0	38.0
14	42.0	42.0	41.7	41.8	42.8	42.8
15	28.7	28.7	26.1	26.2	27.4	27.4
16	26.6	26,6	26.9	27.0	35.5	35.5
17	33.7	33.7	32.5	32.5	43.0	43.0
18	59.0	58.9	47.2	47.4	48.2	48.2
19	39.6	39.6	46.8	46.9	47.9	47.9
20	39.6	39.6	31.1	31.1	151.0	150.9
21	31.2	31.2	34.7	34.8	29.7	29.8
22	41.5	41.5	37.1	37.2	40.0	40.0

23	28.1	28.1	28.1	28.2	27.9	28.0
24	15.5	15.6	15.5	15.5	15.3	15.4
25	15.5	15.6	15.5	15.6	16.1	16.1
26	16.8	16.8	16.8	16.9	15.9	15.9
27	23.3	23.3	26.0	26.0	14.5	14.5
28	28.1	28.1	28.4	28.4	18.0	18.0
29	17.4	17.4	33.3	33.3	109.3	109.3
30	21.4	21.3	23.6	23.7	19.3	19.3

(*) Mahato and Kundu, 1994

Table S3. ^{13}C (125 MHz) NMR data of compound **5**

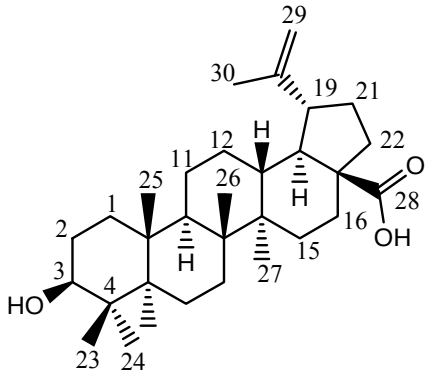


N°C	δ ^{13}C (ppm)	δ ^{13}C (*) (ppm)
1	38.4	38.4
2	27.4	27.4
3	80.6	80.8
4	38.4	38.5
5	55.3	55.3
6	18.0	18.0
7	34.2	34.2
8	55.3	55.4
9	50.3	50.3
10	37.0	37.1
11	20.9	20.9
12	25.0	25.1
13	38.0	38.0
14	42.8	42.1
15	27.4	27.4
16	35.5	35.6
17	48.0	47.8
18	48.2	48.3
19	48.0	48.0
20	150.9	151.0
21	29.8	29.8
22	40.0	40.0
23	27.9	28.1
24	15.7	15.7
25	16.1	16.0

26	15.9	16.2
27	14.5	14.5
28	18.0	18.2
29	109.3	109.3
30	18.2	18.2
1’	171.3	171.0
2’	21.4	21.4

(*) Tsai et *al*., 2012

Table S4. ^{13}C (125 MHz) NMR data of compound **6**

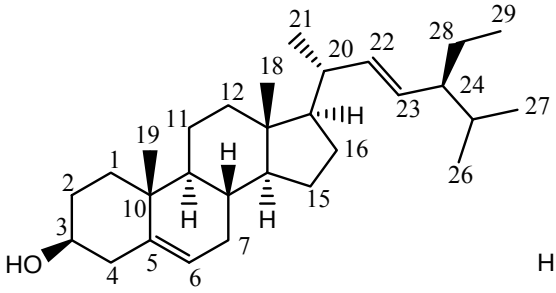


N°C	δ ^{13}C (ppm)	δ ^{13}C (*) (ppm)
1	38.7	38.7
2	27.3	27.4
3	79.0	78.9
4	38.8	38.8
5	55.3	55.3
6	18.2	18.3
7	34.3	34.3
8	40.6	40.7
9	50.5	50.5
10	37.1	37.2
11	20.8	20.8
12	25.4	25.5
13	38.3	38.4
14	42.4	42.4
15	30.5	30.5
16	32.1	32.1
17	56.2	56.3
18	46.8	46.8
19	49.2	49.2
20	150.4	150.3
21	29.7	29.7
22	37.0	37.0
23	27.9	27.9
24	15.3	15.3

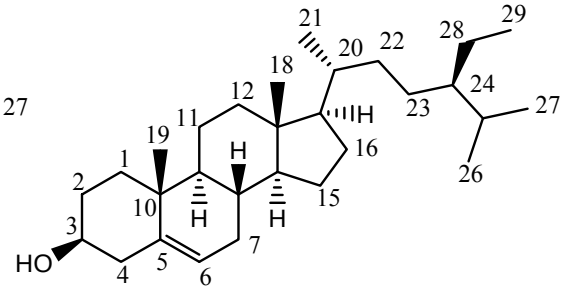
25	16.0	16.0
26	16.1	16.1
27	14.6	14.7
28	180.0	180.5
29	109.7	109.6
30	19.3	19.4

(*) Mahato and Kundu, 1994

Table S5. ^{13}C (125 MHz) NMR data of compounds **7** and **8**



7



8

	7		**8**	
N°C	δ ^{13}C (ppm)	δ ^{13}C (*) (ppm)	δ ^{13}C (ppm)	δ ^{13}C (*) (ppm)
1	37.2	37.2	37.2	37.2
2	31.6	31.6	31.6	31.6
3	71.8	71.8	71.8	71.8
4	42.3	42.1	42.3	42.2
5	140.7	140.7	140.7	140.7
6	121.7	121.7	121.7	121.7
7	31.8	31.8	31.8	31.8
8	31.8	31.9	31.8	31.8
9	50.1	50.1	50.1	50.1
10	36.5	36.4	36.5	36.4
11	21.0	21.0	21.1	21.0
12	39.7	39.7	39.6	39.6
13	42.2	42.2	42.3	42.2
14	56.7	56.7	56.8	56.8
15	24.3	24.2	24.3	24.3
16	28.2	28.2	28.9	28.9
17	56.0	56.0	55.9	55.9
18	11.8	11.8	12.0	12.0
19	19.4	19.3	19.4	19.3
20	36.1	36.1	40.5	40.4
21	18.7	18.7	21.0	21.0
22	33.9	33.9	138.3	138.3

23	26.0	26.0	129.2	129.2
24	45.8	45.8	51.2	51.2
25	29.1	29.1	31.9	31.8
26	19.8	19.8	21.2	21.2
27	18.9	19.0	18.9	18.9
28	23.0	23.0	25.4	25.3
29	11.9	11.9	12.2	12.2

(*) De-Eknamkul and Potduang, 2003