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Review Paper

A review of ^{13}C NMR spectra of drimane sesquiterpenes

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ABSTRACT

Drimane sesquiterpenes are important group of phytochemicals with a wide range of medicinal properties including antibacterial, antifungal, anti-inflammatory, antioxidant, antiplasmodial, antileishmanial, molluscicidal, antifeedant and insecticidal features. Due to their wide range of medicinal activities, scientists are prompted to continuously search for novel drimane sesquiterpenes since most of the currently available anti-infective agents have drawbacks such as drug resistance and side effects. Structure determination of new compounds relies on accurate interpretation of spectroscopic data which is quite challenging but can be simplified by comparison with the data of known related compounds from the reliable databases. A large number of drimane sesquiterpenes have been examined by ^{13}C NMR spectroscopy but such data are scattered in the literature making it hard for researchers to use them. This paper provides a review on previously reported drimane sesquiterpenes and a compilation of their ^{13}C NMR data. It also provides a brief discussion on the substituent effect on the ^{13}C shielding of the drimane sesquiterpenes.

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1. Introduction

The use of medicinal plants as health remedies has been practiced for several thousands of years. In many developing countries, traditional medicine still plays an important role in meeting the primary healthcare needs of the population (WHO, 2014; Mohammadhosseini et al., 2019). Plants produce secondary metabolites that have the capacity to combat numerous types of diseases (Jeruto et al., 2017; Mohammadhosseini et al., 2017; Mohammadhosseini, 2017). Despite the availability of conventional drugs, continued search for novel biologically active compounds is unavoidable since most of the available drugs have demonstrated limitations in terms of side effects and drug resistance (WHO, 2014). Traditional remedies are preferred because they are cheaper and readily available (WHO, 2014). In recent years, many researchers have focused on authenticating the efficacy of medicinal plant extracts through *in-vivo* and in-vitro experiments, and isolation and structural determination of the bioactive compounds (Opiyo et al., 2017; Wansi et al., 2018; 2019). This has led to the identification of several important biologically active compounds including terpenes, alkaloids, steroids, flovonoids and quinones (Ochieng et al., 2013; Ochieng et al., 2017; Ochung et al., 2015; 2018). Such biologically active compounds derived from natural origin represent an important source of drugs in the process of developing new pharmacologically active compounds (Vieira et al., 2014). Drimane sesquiterpenes (**1a**) are C-15 compounds that occur as hydrocarbons or in oxygenated forms such as alcohols, ketones, aldehydes, acids or lactones in nature. Rearranged (**1b**), tricyclic (**1c**) as well as 11-*nor* (**1d**) and 12-*nor* (**1e**) drimanes sesquiterpenes also occur in nature (Fig. 1). Drimane sesquiterpenes are important constituents of essential oils which have various physiological effects. Most of these compounds have nice aroma and are used in soap and perfumery in-

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dustry as well as flavor compounds in aroma mixtures.

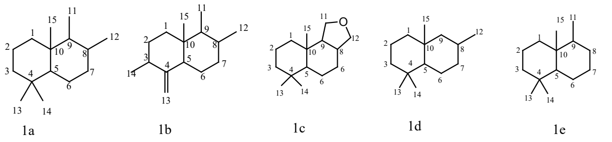


Fig. 1. Structures of drimane sesquiterpenes.

Drimane sesquiterpenes have attracted particular interest because of their numerous potent medicinal properties which include antibacterial (Wube et al., 2005; Opiyo et al., 2011), antifungal (Delgado et al., 2008), antimycobacterial (Wube et al., 2005; Madikane et al., 2007), anti-inflammatory (Cunha et al., 2001; Felix et al., 2014), antioxidant (Jansen and de Groot, 2004), antiplasmodial (Wube et al., 2010; Pittayakhajonwut et al., 2011; Claudino et al., 2013; Nyaba et al., 2018), antileishmanial (Claudino et al., 2013), antifeedant (Kubo and Nakanishi, 1977; Kubo, 1995; Chaudhary et al., 2008; Montenegro et al., 2013; 2018a 2018b; Inocente et al., 2018), molluscicidal (Nakanishi and Kubo, 1978; Kubo et al., 1983; Odyek et al., 1993; Montenegro et al., 2014) and insecticidal properties (Muñoz et al., 2015; Opiyo et al., 2015; Inocente et al., 2018; Montenegro et al., 2018).

1.1. Occurrence of drimane sesquiterpenes

Drimane sesquiterpenoids show a restricted occurrence in a few unrelated lower and higher plants including *Canella winterana* (L.), *Cinnamosma fragrans* (Baill) and *Warburgia ugandensis* Sprague (Table 1). The compounds have been isolated from fungi such as *Phellinus tuberculosis* (Quél.), *Marasmius oreades* (Bolton) Fr., Aspergillus sp. (Micheli.), *Kuehneromyces* sp. (Singer & A.H. Sm.), *Trichopezizella barbata* (Kunze Fr.), *Mniopetalum* sp. (Pers.) *Penicillium brevicompactum* Dierckx, *Lactarius uvidus* (Fr.), *Polyporus* ciliates (Fries), P. *arcularius* Rostk. *Pestalotiopsis* spp. (Steyaert) and *Lepista glaucocana* (Bres.) (Xu et al., 2009a; Felix et al., 2014; He et al., 2015; Chen et al., 2016; Ding et al., 2016; Kunag et al., 2016; Zhao et al., 2017). Drimane sesquiterpenes have also been isolated from marine sponges (Butler and Capon, 1993; Montagnac et al., 1996; Paul et al., 1997). Synthetic drimane sesquiterpenoids have been reported by various coworkers (Lagnel et al., 2000; Jansen and de Groot, 2004; Vlad et al., 2006), as well.

1.2. Structure elucidation

Structure determination of new natural products relies majorly on the acquisition and accurate interpretation of spectroscopic data (Mahato and Kundu, 1994). The assignment of carbon signals of a new compound by comparison with the data of known compounds is simple and straightforward provided that the ^{13}C NMR data of appropriate model compounds are available. A large number of drimane sesquiterpenes have been examined by ^{13}C NMR spectroscopy and considerable ^{13}C NMR chemical shift data have been accumulated. However, these data are scattered in the literature making it hard for researchers to use them. It is therefore necessary to provide an easy access to an extensive list of ^{13}C data of drimane sesquiterpenes.

2. ^{13}C NMR data of drimane sesquiterpenes

This paper provides a compilation of ^{13}C NMR data of selected varieties of naturally occurring and synthetic drimane sesquiterpenes that were previously reported. The sesquiterpenes have been arranged skeleton-wise in the following order: saturated drimane sesquiterpenes **2-24**; drim-8(12)-ene sesquiterpenoids **25-34**; drim-7-ene sesquiterpenes **35-80**; drim-8 (9)-ene sesquiterpenes **81-93**; epoxydrimane derivatives **94-101**; drim-6,8-diene derivatives **102-103**; drim-5,8-diene **104-105**; rearranged drimane sesquiterpenes **106-109**; tricyclic drim-7-enes **110-126**, tricyclic drim-8(9)-enes **127-143**; tricyclic drim-2,8-dienes **144-149**; miscellaneous unsaturated tricyclic drimane sesquiterpenes **150-152**; saturated tricyclic drimane sesquiterpenes **153-158**; rearranged tricyclic drimane sesquiterpenes **159-162** and nordrimane derivatives **163-183**.

2.1. Saturated drimane sesquiterpenes

Several groups of researchers have assigned the ^{13}C resonances of a variety of saturated drimane sesquiterpene consisting of monohydro **2-4**, **6**, **18**, **21**, dihydro **7**, **8**, trihydro **5**, **9-13**, **15-17**, and tetrahydro drimane derivatives (Table 2). The ^{13}C NMR values of representative saturated drimanes **2-24** are summarized in Table 3 (Montagnac et al., 1996; Meng et al., 2011; Yonemura et al., 2012; Derita et al., 2013; Skiredj, 2016). Most of the compounds have hydroxyl groups attached to C-6, C-7, C-8, C-11 and C-12 (Barrero et al., 1995; Lagnel et al., 2000; Benites et al., 2001; Panasenko et al., 2004; Yonemura et al., 2012; He et al., 2015; Skiredj, 2016). Compounds **14-17** have hydroxyl group attached to C-3 (Meng et al., 2011; He et al., 2015). Mono and di-acetylated derivatives **19, 21-24** have been reported. In most cases, the acetyl substitution occurs at C-8, C-11 and C-12 (Barrero et al., 1995; Lagnel et al., 2000; Benites et al., 2001).

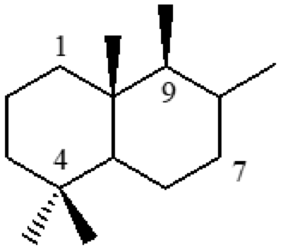
Table 1

Some plants sources of drimane sesquiterpenes.

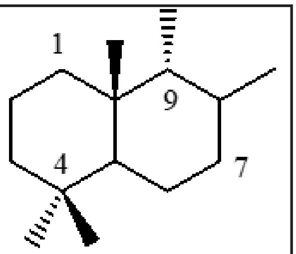
Family	Plant species	Reference
Amaranthaceae	*Tidestromia oblongifolis* (S. Watson) Standl	Chaudhary et al., 2008
Apiaceae	*Heptaptera anatolica* (Boiss.) Tutin	Tosun et al., 2019
	Heptaptera anisoptera Tutin	Appendino et al., 1992
Asteraceae	*Tanacetum heterotomum* (Bornm.)	Gören and Ulubelen, 1988
	Tanacetum parthenium L.	Kisiel and Stojakowska, 2002
Canellaceae	*Canella winterana* (L.) Gaertn.	Grace et al., 2010
	Cinnamodendron corticosum (Miers)	Seeram et al., 2003
	Cinnamosma fragrans (Baill)	Inocente et al., 2018
	Warburgia salutaris (Bertol. f.) Chiov	Nyaba et al., 2018
	Warburgia stuhlmannii Engl.	Kioy et al., 1990
	Warburgia ugandensis Sprague	Opiyo et al., 2011
	Capsicodendron dinisii (Schwacke) Occhioni	Bastos et al., 1999
Cinnamosma	*Cinnamosma madagascariensis* Danguy	Harinantenaina et al., 2008
Makinoaceae	*Makinoa crispate (Stephani)* Miyake	Hashimoto et al., 1989
Polygonaceae	*Polygonum hydropiper* Linn.	Sultana et al., 2011
	Polygonum glabrum Willdenow	Jacobsson and Muddathir, 1992
	Polygonum punctatum (Elliott)	Alves et al., 2001
Porellaceae	*Porella acutifolia* (Lehm. & Lindenb.) Trevis	Ludwiczuka et al., 2011
	Porella canariensis (F. Weber) Underw	Ludwiczuka et al., 2011
	Porella cordeana (Hiib.) Evs.	Ludwiczuka et al., 2011
	Porella navicularis (Lehm. & Lindenb.) Lindb.	Ludwiczuka et al., 2011
	Porella vernicosa Lindb.	Ludwiczuka et al., 2011
Scapaniaceae	*Diplophyllum serrulatum* (K. Müller)	Toyota et al., 1994
Solanaceae	*Nicotiana tabacum* L.	Hlubucel et al., 1974
Umbelliferae	*Ferula assa-foetida* L.	Lee et al., 2009
	Ferula gummosa Boiss.	Iranshahi et al., 2014
Winteraceae	*Drimys arfakensis* (Gibbs.)	Santoso et al., 2018
	Drimys brasiliensis Miers	Claudino et al., 2013
	Drymus winteri (J.R. Forst. & G. Forst.)	Muñoz et al., 2015
	Pseudowintera colorata (Raoul) Dandy	Wayman et al., 2010
	Pseudowintera insperata Heenan et de Lange	Wayman et al., 2010
	Tasmannia lanceolata R.Br.	Mathie et al., 2017
Zingiberaceae	*Hedychium spicatum* (Buch.) Ham.	Reddy et al., 2009

Table 2

Structures of drimanes **2-24.**



For cpds 2, 3, 5-12, 14-24



For cpds 4 & 13

2 8α-OH
3 8β-OH, driman-8β-ol
4 8β-OH, isodriman-8β-ol
5 7β, 8β, 9α-OH
6 11-OH, 14 3β, 8α,
7 11, 12-OH
8 8α, 11-OH
9 7β, 8β, 11- OH

10 7α, 8α, 11-OH
11 6α, 8α, 11-OH
12 9α, 11, 12-OH
13 8α, 11, 12-OH
11, 12-OH
15 3β, 8β, 11, 12 -OH, sulphureuine B
16 3α, 8β, 11, 12-OH, sulphureuine C
17 3β, 11, 12-OH, sulphureuine G

18 8α-OH, 11-CHO
19 6α, 8α-OAc, 11-CHO
20 8α-COOH, 11-CHO
21 8α-OH, 11-OAc
22 11, 12-OAc
23 8α-OAc, 11-COOH
24 8α-OAc, 11-COOMe

Non-substituted drimane sesquiterpene (**1a**) consists of five methyl (C-11, C-12, C-13, C-14 & C-15), five methylene (C-1, C-2, C3, C-6 & C-7), three methine (C-5, C-8 & C-9) and two quaternary (C-4 & C-10) carbon atoms. The ^{13}C NMR chemical shifts for all the 15 carbon in a non-substituted drimane range between δ 7-60 ppm. Substitution affects the chemical shifts of adjacent and nearby nuclei. Inspection of the ^{13}C NMR data of various mono- and polyhydroxy drimanes sesquiterpenes (Table 3) reveals that introduction of a hydroxyl group results in downfield shifts of 34-50 ppm for α-carbons and 2-10 ppm for β-carbons and upfield shifts of 0-9 ppm for γ-carbons. Generally, hydroxylated carbon atoms at C-3, C-7 & C-8 resonate between δ 71-85 ppm, while those at C-6, C-11 & C-12 resonate between δ 59-70 ppm. In polyhydroxy drimanes such as in 1,2- or 1,3-dihydroxy derivatives, there is additivity of the substituent effect on chemical shifts of the nuclei that explains, for example, why C-8 in compound 5 resonates more downfield than that in isodriman-8β-ol (**4**). Acetylation of the hydroxyl group enhances the α-effect and diminishes the β-effect. However, the γ-effect remains more or less unaltered. The effect at β-position is attributed to the γ-effect of the acetyl moiety (Mahato and Kundu, 1994). For example, in driman-8,11-diol (**8**) and 11-acetoxydriman-8α-ol (**21**), C-11, C-9 and C-10 resonate at δ 61.0, 60.5, 37.5 and 62.6 (+1.6), 59.4 (-1.1), 38.1 (+0.6) ppm, respectively. The substituent effects depend on the degree of substitution of carbon under consideration as follows: quaternary carbons < methine carbons < methylene carbons (Mahato and Kundu, 1994). The configuration at C-9 in a drimane sesquiterpene can be α or β and the difference can be observed considering the chemical shift of γ- carbons at C-1, C-5 and C-15 (Rodriguez et al., 2005). For example, driman-8β-ol (**3**) and isodriman-8β-ol (**4**) are epimers at the C-9 stereogenic center and the configuration of the C-11 methyl substituent is evidenced by the noticeable difference in the chemical shifts of the C-1, C-5 and C-15γ carbons [Δδ = δ(**3**) - δ(**4**): +2.9, +10.5 and -9.6 ppm, respectively]. The presence of 1,3-diaxial interactions results in less shielding of nuclei as in the case of methyl C-11 carbon in compound **4** which results to a downfield shift by ~4.7 ppm (Table 3).

2.2. Drim-8(12)-ene sesquiterpenes

Compounds **25-34** (Table 4) are examples of some previously reported drimane sesquiterpenes. Generally, their olefinic carbons C-8 and C-12 resonate between δ 143.1-161.5 and δ 106.3-109.9 ppm, respectively (Aasen et al., 1977; Barrero et al., 1995; Kinoshita et al., 2002; Justicia et al., 2005; Delgado et al., 2008; Xu et al., 2009a). In drim-8(12)-enes with no substituents in close proximity to the 8:12 double bond, the chemical shifts of the olefinic C-8 and C-12 carbons are ~151 and ~101 ppm, respectively. However, the presence of an additional double bond (conjugation) has a pronounced effect on the olefinic carbons resonances. For example, the olefinic carbons C-8 and C-12 in drimanes such as drim-8(12),9(11)-diene (26) resonate more downfield at δ 161.5 and 108.8 ppm, respectively, i.e. the olefinic carbons are deshielded by 10.0 ppm and 7.3 ppm for C-8 and C-12, respectively (Table 3). The additional olefinic carbon atoms in compound **26** resonate at δ 149.9 and 103.0 ppm for C-9 and C-11, respectively (Kinoshita et al., 2002). The presence of a hydroxyl group at C-11 cause characteristic downfield (~5 ppm) and upfield shifts (~ 4 ppm) for the olefinic C-l2 and C-8, respectively. In the presence of two hydroxyl groups (at C-7 and C-11), the olefinic carbon C-12 is further deshielded, while C-8 becomes shielded (cf. drimanes **25**, **27** and **28**). Acetylation of the hydroxyl group at C-11 further deshields C-12 but shields C-8 as evidenced by ^{13}C shifts of drimanes **27** and **30**. Mono and di-acetylated derivatives of 8(12)-drimenes such as **29-34** having the acetyl group mostly at C-3 or C-11 were reported (Barrero et al., 1995; Toshima et al., 2001; Justicia et al., 2005; Dacunto, 2012; Derita et al., 2013).

Table 3

^{13}C NMR data of drimane sesquiterpenes.

C	2^C	3^A	4^C	5^C	6^C	7^C	8^C	9^C	10^C
1	39.9	40.8	37.9	32.9	39.9	39.4	40.0	40.1	39.6
2	18.7	19.3	18.8	18.3	17.5	18.5	18.6	18.4	18.6
3	42.0	42.8	42.7	41.5	41.9	41.9	41.7	41.7	40.8
4	33.3	33.9	33.2	33.2	33.2	33.2	33.2	33.2	32.7
5	56.2	56.9	46.4	43.7	56.5	56.4	55.9	52.4	45.1
6	20.5	19.3	18.8	27.7	18.4	18.3	20.1	27.7	25.7
7	44.5	43.6	35.6	73.5	34.5	30.0	44.3	76.6	74.0
8	73.1	71.8	74.9	77.3	28.5	37.9	75.0	75.7	75.3
9	55.6	53.6	53.5	78.9	55.7	54.5	60.5	57.8	54.4
10	37.8	38.7	37.4	42.2	37.6	37.3	37.5	38.1	37.0
11	7.4	7.9	12.6	17.6	61.0	60.4	61.0	59.8	60.8
12	23.1	31.4	32.4	21.8	15.6	66.4	24.2	25.8	23.1
13	33.5	34.0	33.5	21.8	21.6	33.5	33.5	21.6	21.6
14	21.6	22.2	22.0	33.6	33.6	21.6	21.6	33.6	32.3
15	14.4	14.9	24.5	17.1	17.1	16.4	16.0	16.7	15.6
Ref	Wahlberg et al., 1981	Yonemura et al., 2012	Ohloff and Giersch, 1985	Panasenko et al., 2004	Derita et al., 2013	Benites et al., 2001	Barrero et al., 1995	Panasenko et al., 2004	Panasenko et al., 2004

Table 3 Continued

C	11^{C}	12	13^{C}	14^{C}	15^{D}	16^{D}	17^{D}	18^{C}	19^{C}	20^{C}
1	40.2	31.5	37.4	38.1	37.8	32.4	37.5	40.0	43.3	40.2
2	18.4	18.7	18.8	26.6	27.0	25.2	27.1	18.3	17.6	19.0
3	43.1	41.5	42.1	77.8	76.9	73.7	76.7	42.9	39.7	42.5
4	33.7	33.4	33.4	38.6	38.6	37.2	38.6	33.4	33.0	34.0
5	59.8	46.1	56.9	55.3	54.2	49.7	55.0	41.8	56.3	54.9
6	68.6	21.2	20.0	19.2	17.5	17.3	17.2	20.0	69.1	21.8
7	36.3	26.1	33.1	36.7	36.9	36.9	28.6	40.0	45.6	30.2
8	74.5	42.9	76.4	75.1	73.7	74.0	37.7	71.4	81.9	40.2
9	61.1	75.4	48.6	60.4	54.1	55.9	55.2	55.3	67.4	64.4
10	38.2	41.5	37.6	37.1	37.1	37.1	36.5	37.5	38.2	38.9
11	53.9	63.6	60.9	58.7	57.4	57.4	58.3	208.3	202.0	210.9
12	22.3	64.9	69.5	63.6	68.8	68.8	59.3	25.4	21.0	182.9
13	33.7	22.1	21.8	27.3	16.5	16.5	16.3	33.5	35.5	34.2
14	25.7	33.6	23.7	14.7	16.0	22.2	15.8	21.5	22.9	22.2
15	18.2	15.4	33.0	15.9	28.6	28.9	28.3	17.7	17.6	16.6
16	-	-	-	-	-	-	-	-	169.1	-
17	-	-	-	-	-	-	-	-	21.7	-
18	-	-	-	-	-	-	-	-	169.1	-
19	-	-	-	-	-	-	-	-	21.8	-
Ref.	Lagnel et al., 2000	Benites et al., 2001	Derita et al., 2013	Meng et al., 2011	He et al., 2015	He et al., 2015	He et al., 2015	Skiredj, 2016	Lagnel et al., 2000	Montagnac et al., 1996

Table 3 Continued

C	**21^C**	**22^C**	**23^C**	**24^C**	**25^B**	**26^C**	**27^C**	**28^C**	**29^C**	**30^C**
1	39.7	39.1	39.7	39.7	39.5	42.4	39.1	38.9	37.6	39.1
2	18.4	18.4	18.2	18.2	19.6	19.3	19.2	19.3	23.6	19.3
3	41.7	41.8	41.7	41.8	42.4	37.6	41.9	42.0	80.5	42.0
4	33.2	33.3	33.1	33.1	33.5	33.9	33.5	33.1	38.1	33.6
5	55.7	56.2	55.1	55.1	55.4	52.6	55.2	47.4	54.5	54.8
6	20.3	17.6	20.1	20.1	24.2	22.8	24.2	30.4	24.2	24.0
7	43.9	29.1	38.7	38.9	37.7	36.0	37.9	73.6	36.7	37.7
8	72.6	34.9	85.0	85.2	151.5	161.5	147.9	148.4	147.1	146.7
9	59.4	51.4	63.0	63.4	50.5	149.9	59.1	53.2	58.8	55.1
10	38.1	37.1	38.4	38.6	39.0	40.3	39.0	39.2	38.6	39.0
11	62.6	62.6	172.5	172.5	10.6	103.0	58.8	58.3	58.8	61.6
12	24.6	63.9	22.6	22.6	101.5	108.8	106.3	109.9	107.0	107.1
13	33.4	33.4	33.3	33.2	33.7	22.2	33.6	33.4	28.31	33.7
14	21.5	21.5	21.3	21.3	22.0	33.5	21.8	21.6	16.7	21.9
15	15.8	16.4	15.2	15.3	13.5	20.8	15.3	14.4	15.4	15.2
16	171.3	171.1	170.0	169.6	-	-	-	-	171.0	171.2
17	21.3	21.0	20.8	20.9	-	-	-	-	21.3	21.2
18	-	171.1	-	50.9	-	-	-	-	-	-
19	-	21.0	-	-	-	-	-	-	-	-
Ref.	Barrero et al., 1995	Benites et al., 2001	Barrero et al., 1995	Barrero et al., 1995	Yonemura et al., 2012	Kinoshita et al., 2002	Delgado et al., 2008	Barrero et al., 1995	Justicia et al., 2005	Toshima et al., 2001

Table 3 Continued

C	**31^{C}**	**32^{C}**	**33^{C}**	**34^{C}**	**35^{C}**	**36^{C}**	**37^{C}**	**38^{M}**	**39^{C}**	**40^{B}**
1	38.6	37.2	37.3	36.5	39.4	36.8	34.5	38.9	39.3	39.8
2	19.2	23.7	23.4	22.7	18.8	21.7	38.5	28.1	18.2	19.3
3	42.0	78.8	80.4	80.5	42.2	42.7	216.7	79.6	43.0	42.6
4	33.1	38.9	38.1	38.0	32.9	33.0	47.5	39.7	32.3	33.0
5	47.2	54.5	54.4	53.9	40.9	57.6	51.1	51.0	58.2	50.4
6	30.6	27.9	24.2	24.0	23.6	24.0	23.8	24.2	200.3	24.1
7	73.7	27.6	36.7	35.8	123.9	124.6	123.7	123.7	129.0	121.9
8	148.2	146.4	146.1	143.1	133.0	131.1	132.9	134.9	157.5	135.3
9	49.4	54.7	54.4	62.5	57.3	43.4	56.0	58.2	63.0	49.0
10	39.2	39.4	38.6	38.8	36.1	36.1	35.8	36.8	42.1	36.0
11	61.4	61.7	61.5	165.6	60.9	61.3	60.6	61.2	59.9	11.6
12	110.5	107.8	107.7	108.9	21.9	22.2	21.7	22.2	21.7	22.0
13	33.4	28.5	28.30	28.2	33.4	33.2	25.2	28.7	33.6	33.5
14	20.4	15.7	16.6	16.6	22.0	23.0	22.3	15.9	22.0	22.1
15	14.2	15.5	15.2	14.3	12.8	18.8	14.5	14.9	15.9	13.5
16	171.4	171.6	171.2	171.8	-	-	-	-	-	-
17	20.9	21.3	21.3	21.3	-	-	-	-	-	-
18	-	-	170.9	51.0	-	-	-	-	-	-
19	-	-	21.1	-	-	-	-	-	-	-
Ref.	Barrero et al., 1995	Dacunto, 2012	Justicia et al., 2005	Justicia et al., 2005	Aasen et al., 1977	Derita et al., 2013	Xu et al., 2009a	Xu et al., 2009a	Lagnel et al., 2000	Yonemura et al., 2012

Table 3 Continued

C	**41^{C}**	42^{C}	**43^{C}**	**44^{A}**	**45^{C}**	**46^{C}**	**47^{D}**	**48^{D}**	**49^{C}**	**50**
1	40.4	31.6	42.4	33.2	31.6	37.8	29.6	41.0	39.1	27.3
2	18.3	18.6	18.4	19.5	18.0	20.4	26.3	62.4	18.1	37.6
3	42.0	41.8	42.6	45.2	42.6	43.1	76.7	51.7	42.9	78.9
4	33.0	32.1	34.6	34.8	32.2	32.8	37.1	33.4	32.2	38.7
5	49.1	42.9	50.3	47.2	55.7	61.1	55.3	54.7	54.6	49.3
6	23.7	24.1	68.4	65.4	200.2	199.6	199.5	199.6	199.6	23.2
7	125.5	127.5	124.3	129.4	129.2	128.0	128.2	128.1	129.4	123.5
8	127.8	135.3	128.9	137.7	154.9	156.2	157.5	157.6	155.4	132.3
9	67.6	75.6	76.0	75.4	74.7	150.0	74.6	74.6	63.0	53.2
10	37.0	40.7	38.1	41.2	45.0	42.9	44.5	46.2	42.2	35.7
11	206.7	62.4	59.0	62.8	61.8	111.8	61.7	61.9	61.7	63.0
12	21.6	20.3	20.1	20.5	20.0	21.8	19.2	19.3	21.1	21.5
13	22.1	33.5	32.4	18.9	21.8	33.3	18.1	18.9	33.5	14.5
14	33.3	22.3	22.4	25.3	33.7	23.3	28.9	33.8	21.7	15.2
15	15.7	15.3	18.2	33.4	17.7	18.4	15.5	22.7	15.6	28.0
16	-	-	-	-	-	-	-	-	170.8	171.2
17	-	-	-	-	-	-	-	-	21.6	21.3
Ref.	Barrero et al., 1999	Barrero et al., 1999	Lagnel et al., 2000	Grabley et al., 1996	Panasenko et al., 2004	Lagnel et al., 2000	Lu et al., 2009	Lu et al., 2009	Lagnel et al., 2000	Ramirez et al., 1993

Table 3 Continued

C	**51^{C}**	**52^{C}**	**53^{C}**	**54^{C}**	**55^{M}**	**56^{A}**	**57^{M}**	**58^{M}**	**59^{C}**	**60^{C}**
1	27.4	39.5	49.5	36.5	38.8	35.1	38.9	39.0	39.5	79.8
2	37.7	18.8	65.3	18.8	28.1	38.7	28.6	28.8	18.0	24.8
3	78.9	42.0	51.7	42.7	79.5	215.1	79.5	79.7	41.7	39.6
4	38.8	33.0	35.4	33.1	39.8	47.9	39.8	39.9	33.0	32.8
5	49.4	49.4	50.5	54.1	50.7	51.8	50.7	50.8	48.9	48.5
6	23.3	23.6	24.4	24.3	24.3	24.4	24.2	24.5	25.2	27.8
7	124.1	127.5	126.4	127.5	126.4	125.0	126.7	129.1	154.4	153.1
8	131.8	137.0	138.4	137.2	138.4	139.3	137.2	134.3	138.1	139.5
9	53.3	54.5	55.9	43.4	55.8	54.7	52.1	55.8	60.2	59.8
10	35.9	35.7	38.5	35.9	36.6	36.2	36.9	36.8	36.8	43.5
11	64.3	61.5	61.2	63.1	61.2	60.9	63.5	60.9	201.9	203.9
12	21.7	67.5	66.8	67.7	67.0	66.7	65.7	68.7	193.2	192.9
13	14.7	33.2	23.2	21.7	15.0	14.4,	15.1	15.0	33.1	32.7
14	15.4	21.9	33.8	22.0	15.9	22.5	15.9	15.0	21.9	22.0
15	28.2	14.6	15.9	33.0	28.7	25.7	28.0	28.2	15.1	9.3
16	173.5	-	-	-	-	-	172.9	173.0	-	-
17	60.9	-	-	-	-	-	21.1	21.1	-	-
Ref.	Zhao et al., 2014	Aasen et al., 1977	Xiao et al., 2017	Derita et al., 2013	Aranda et al., 1992	Zhao et al., 2014	He et al., 2014	He et al., 2014	Santoso et al., 2018	Dacunto, 2012

Table 3 Continued

C	**61^{C}**	**62^{C}**	**63^{C}**	**64^{I}**	**65^{D}**	**66^{C}**	**67^{P}**	**68^{C}**	**69^{C}**	70^{C}
1	37.3	37.0	37.1	74.7	37.2	31.7	42.4	31.9	36.5	31.1
2	25.0	23.2	18.3	25.3	18.1	18.3	32.6	19.9	18.5	18.6
3	78.3	79.7	42.0	39.6	41.8	41.8	17.3	44.2	41.8	41.6
4	36.5	36.4	32.8	32.7	32.6	33.5	36.2	34.0	33.2	33.0
5	48.4	48.6	44.1	43.6	43.1	42.2	47.9	45.2	47.6	42.3
6	26.7	24.7	25.5	27.5	24.4	26.5	67.2	66.2	25.7	24.1
7	154.0	153.3	153.5	152.7	142.3	158.3	158.7	148.5	152.2	131.8
8	138.1	138.2	137.3	137.5	126.3	141.0	139.3	141.3	136.4	138.2
9	60.0	59.9	58.4	54.9	60.6	78.3	77.6	77.5	149.2	75.7
10	38.8	37.7	37.6	43.1	36.7	42.0	43.1	41.7	37.4	40.5
11	201.6	201.3	202.3	203.1	203.7	203.0	202.5	201.0	193.6	62.6
12	193.0	192.9	192.8	192.9	167.5	193.4	192.3	192.9	109.4	66.9
13	27.9	27.9	32.7	32.3	32.5	33.5	17.1	32.6	32.4	30.9
14	15.4	16.5	21.8	22.1	21.4	22.6	21.9	24.7	21.6	22.3
15	15.2	16.5	21.4	14.8	21.1	17.6	35.8	17.7	19.8	15.3
16	-	170.7	-	-	-	-	-	170.0	-	-
17	-	21.2	-	-	-	-	-	21.3	-	-
Ref.	Dacunto, 2012	Dacunto, 2012	Rodriguez et al., 2005	Dacunto, 2012	Liu et al., 2010	Mashimbye et al., 1999	Kioy et al., 1989	Mahmoud et al., 1980	Jansen, 1993	Barrero et al., 1999

Table 3 Continued

C	**71^{M}**	**72^{D}**	**73^{C}**	**74**	**75^{M}**	**76^{M}**	**77^{M}**	**78^{C}**	**79^{M}**	**80^{M}**
1	33.6	32.2	39.4	40.1	38.8	38.9	38.8	39.1	38.6	38.7
2	19.8	18.2	18.6	18.6	28.8	28.8	28.7	39.1	27.8	27.7
3	45.6	43.1	41.9	42.0	81.4	81.3	81.3	35.5	73.7	73.5
4	35.1	32.8	32.8	33.2	43.1	43.1	43.0	35.6	43.6	43.6
5	47.5	45.7	49.4	49.5	51.7	51.6	51.1	42.8	43.0	43.0
6	65.5	77.1	23.3	24.8	24.4	24.4	24.5	23.6	24.0	24.0
7	131.0	125.1	126.4	151.0	126.2	126.7	128.8	127.3	126.3	126.7
8	140.8	140.6	136.0	139.1	138.7	137.4	134.4	137.3	138.5	137.2
9	76.6	74.4	50.5	55.3	55.8	52.2	55.7	54.7	55.7	52.1
10	41.6	42.0	35.7	35.7	36.5	36.8	36.6	34.8	36.4	36.7
11	63.4	61.9	63.1	176.6	61.3	63.6	60.9	61.6	61.4	63.6
12	64.7	61.1	65.9	192.6	66.8	65.8	68.6	67.7	67.0	65.9
13	19.4	17.5	33.1	33.3	16.1	16.1	16.0	71.8	15.7	15.8
14	25.3	36.2	21.8	22.1	65.0	65.0	65.0	18.0	12.6	12.6
15	33.5	23.3	14.3	15.2	23.3	23.3	23.3	15.3	66.6	66.5
16	-	53.8,	170.7	-	-	173.0	173.0	-	-	173.0
17	-	-	21.0	-	-	21.2	21.1	-	-	21.2
Ref.	Grabley et al., 1996	Lu et al., 2009	Barrero et al., 1995	Fukuyama et al., 1985	He et al., 2014	He et al., 2014	He et al., 2014	Chaudhary et al., 2008	He et al., 2014	He et al., 2014

Table 3 Continued

C	81^c	82^c	83^c	84^c	85^c	86^c	87^c	88^c	89^c	90^c
1	37.3	36.2	36.9	35.5	34.9	35.6	36.2	36.3	35.4	36.0
2	19.5	18.7	19.0	18.5	18.7	18.6	18.9	18.9	18.5	18.6
3	42.0	41.2	41.8	41.1	41.0	41.2	41.5	41.6	41.1	41.3
4	33.4	33.0	33.3	33.0	33.1	32.8	33.3	33.3	33.1	32.8
5	51.9	50.0	51.8	50.2	50.0	49.6	51.3	51.4	50.1	49.6
6	19.5	35.2	19.0	35.5	35.0	29.4	18.7	18.8	35.3	29.5
7	34.1	199.9	33.8	201.2	201.0	75.1	31.3	33.8	200.4	72.8
8	124.3	129.3	132.5	132.4	134.7	136.4	136.0	135.3	134.5	136.8
9	136.2	165.3	141.1	162.8	169.5	150.5	146.2	135.5	158.2	138.7
10	38.5	40.4	38.1	39.9	40.2	39.3	38.2	38.0	40.0	38.9
11	19.8	14.9	58.4	58.5	58.1	57.9	57.9	60.7	60.0	60.4
12	19.8	11.9	21.7	11.3	56.5	61.1	64.0	21.3	11.5	21.5
13	33.4	21,2	33.3	21.2	21.1	21.5	20.4	33.3	32.5	33.0
14	21.8	32.5	20.8	32.5	32.4	33.0	33.2	21.6	21.2	21.1
15	19.5	17.5	19.4	18.3	18.0	20.0	21.6	19.5	18.3	15.0
16	-	-	-	-	-	-	-	-	170.7	171.0
17	-	-	-	-	-	-	-	20.7	20.9	20.5
Ref.	Yonemura et al., 2012	Panasenko et al., 2004	Kuchkova et al., 2005	Panasenko et al., 2004	Panasenko et al., 2004	Panasenko et al., 2004	Benites et al., 2001	Barrero et al., 1999	Barrero et al., 1999	Barrero et al., 1999

Table 3 Continued

C	91[c]	92[c]	93[c]	94[c]	95[c]	96[c]	97[c]	98[c]	99	100
1	35.6	42.3	40.7	35.1	34.6	34.5	35.7	37.4	40.5	39.2
2	18.5	18.6	18.9	18.5	18.5	18.3	18.5	18.4	17.8	27.3
3	41.1	42.9	43.5	41.1	42.0	41.3	41.2	42.7	42.6	78.3
4	32.9	33.1	33.4	33.2	32.7	32.9	33.3	33.5	32.2	38.3
5	42.2	53.2	54.0	41.7	40.0	43.3	41.9	47.6	65.0	64.6
6	28.6	69.2	70.5	35.9	28.6	17.2	34.7	68.6	204.7	205.0
7	69.7	36.0	36.9	209.4	70.2	25.9	207.7	35.3	60.7	62.1
8	135.3	142.9	129.2	65.8	64.8	65.6	66.5	62.4	61.4	62.5
9	145.0	147.7	140.9	72.4	71.0	72.1	73.2	69.6	55.2	55.8
10	39.4	40.1	36.9	37.9	37.9	37.3	37.7	38.1	37.2	37.6
11	59.2	190.7	57.8	12.3	13.9	61.4	58.5	58.1	60.5	60.6
12	61.2	21.1	21.9	12.3	16.8	66.0	12.4	20.1	21.5	21.8
13	21.5	36.0	36.2	20.6	21.2	21.5	32.5	35.0	33.2	28.5
14	32.9	21.2	22.3	32.4	33.5	33.6	20.7	22.4	21.6	15.6
15	20.4	17.7	18.7	17.0	17.7	16.4	17.1	18.2	18.7	19.0
16	170.8	169.3	169.7	-	-	-	-	169.8	-	-
17	21.1	21.0	21.4	-	-	-	-	21.3	-	-
18	171.4	-	-	-	-	-	-	-	-	-
19	21.1	-	-	-	-	-	-	-	-	-
Ref.	Panasenko et al., 2004	Lagnel et al., 2000	Lagnel et al., 2000	Panasenko et AL., 2004	Panasenko et al., 2004	Benites et al., 2001	Barrero et al., 1999	Lagnel et al., 2000	De Bernardi et al., 1980	De Bernardi et al., 1980

Table 3 Continued

C	**101^C**	**102^C**	**103^C**	**104^C**	**105^C**	**106^D**	**107^C**	**108^C**	**109**	**110^C**
1	43.2	40.7	32.1	34.3	33.9	36.1	31.7	39.4	31.7	39.3
2	18.8	18.8	18.4	18.0	17.9	29.8	30.8	31.6	31.8	18.8
3	44.5	35.1	38.6	40.3	40.0	39.7	38.1	38.5	38.8	42.0
4	34.3	31.9	32.8	37.4	37.5	155.6	151.8	151.3	149.1	32.9
5	54.3	52.6	51.2	172.6	173.1	47.7	40.1	45.8	50.4	49.4
6	63.2	136.5	115.6	123.8	124.1	23.5	27.7	27.0	66.1	23.6
7	65.2	130.2	129.0	186.9	185.3	36.7	151.8	152.9	153.7	127.4
8	63.2	144.2	139.7	135.2	133.3	76.8	139.6	137.9	139.3	136.9
9	55.2	142.9	146.8	154.7	160.4	59.7	77.4	58.3	77.6	54.4
10	35.7	39.1	40.5	43.3	43.8	40.6	42.2	38.2	44.1	35.6
11	60.8	190.8	59.7	60.2	59.4	60.7	201.3	201.1	200.5	61.4
12	22.6	22.5	11.9	11.0	57.2	65.0	192.7	193.3	192.6	67.4
13	33.3	32.4	34.4	28.3	28.6	106.9	106.0	106.0	106.7	33.2
14	24.7	22.5	22.5	32.3	31.7	20.6	15.1	18.4	18.2	21.9
15	19.0	15.8	15.7	25.1	25.4	14.4	18.1	13.5	15.8	14.5
16	-	-	169.3	170.7	170.3	-	-	-	-	-
17	-	-	20.4	20.7	20.6	-	-	-	-	-
18	-	-	170.7	-	170.8	-	-	-	-	-
19	-	-	20.8	-	20.9	-	-	-	-	-
Ref.	Lagnel et al., 2000	Lignel et al., 2000	Vlad et al., 2006	Vlad et al., 2006	Vlad et al., 2006	He et al., 2015	Mashimbye et al., 1999	Mashimbye et al., 1999	Wube et al., 2005	Derita et al., 2013

Table 3 Continued

C	111^{C}	112^{A}	113^{C}	114^{C}	115^{C}	116^{A}	117^{C}	118^{C}	119^{M}	120^{M}
1	38.5	31.3	37.6	39.8	33.4	49.9	30.5	47.4	25.1	25.9
2	18.3	25.8	27.1	18.5	18.1	64.0	17.8	66.0	25.7	25.2
3	42.4	75.5	79.0	42.4	35.8	52.4	44.7	55.2	76.7	78.7
4	33.1	37.9	38.8	32.9	38.0	35.0	34.1	37.2	38.9	39.3
5	49.7	43.6	49.2	49.8	50.8	50.2	45.6	50.6	37.6	41.4
6	23.4	23.5	23.5	23.6	23.2	24.2	65.4	66.2	24.8	66.4
7	121.2	121.3	116.9	117.1	117.0	116.8	127.8	129.5	122.9	124.8
8	129.9	131.6	136.3	136.5	136.6	138.4	132.8	135.1	139.0	140.1
9	53.7	54.0	61.4	61.6	61.8	62.5	74.9	76.2	78.5	78.5
10	34.4	34.5	33.2	33.4	39.0	35.6	37.6	40.9	38.2	38.8
11	175.2	175.5	99.2	99.4	99.4	99.5	175.3	177.8	99.1	99.3
12	69.8	70.2	68.8	68.9	69.0	68.5	69.1	70.9	68.2	67.9
13	21.4	22.1	14.9	33.1	26.6	22.7	32.6	33.8	22.9	25.6
14	33.0	28.7	27.7	21.5	64.8	33.5	25.0	26.8	29.1	28.4
15	13.9	14.3	14.1	14.0	15.0	15.2	18.9	20.8	16.5	19.4
Ref.	Rukachaisirikul et al., 2010	Kuang et al., 2016	Echeverri et al., 1997	Derita et al., 2013	Ayer and Craw, 1989	Kuang et al., 2016	Shiono et al., 2007	Shiono et al., 2007	Yang et al., 2013	Yang et al., 2013

Table 3 Continued

C	**121^{C}**	**122^{C}**	**123^{A}**	**124^{C}**	**125^{DC}**	**126^{C}**	**127^{M}**	**128^{M}**	**129^{C}**	**130^{C}**
1	39.1	36.9	37.9	41.6	30.3	31.9	34.2	74.7	33.5	35.4
2	18.2	23.5	27.9	17.9	17.5	19.6	27.1	22.3	17.9	18.3
3	41.9	80.2	78.3	31.3	41.1	44.5	78.3	35.1	40.5	41.7
4	33.9	37.7	39.4	32.7	33.0	33.6	39.0	33.4	32.7	33.5
5	50.5	49.4	49.6	41.7	41.1	44.9	50.6	45.2	52.3	51.5
6	24.7	24.7	25.2	25.3	25.2	67.3	18.1	17.7	117.6	18.0
7	135.9	135.7	135.5	141.1	143.3	134.9	21.6	21.6	131.7	21.5
8	127.0	127.2	129.7	130.0	129.2	131.5	123.8	129.7	122.3	128.3
9	49.4	50.6	59.7	77.3	75.7	76.7	170.0	164.9	171.7	167.7
10	32.8	34.1	34.4	38.5	39.2	38.9	36.4	40.8	36.8	37.0
11	66.9	66.9	99.5	74.3	98.5	104.3	68.2	97.2	67.7	99.1
12	169.8	169.7	167.6	169.3	168.7	104.1	174.7	171.4	170.2	172.0
13	32.5	15.9	15.4	17.0	16.1	32.9	15.6	21.5	32.3	20.3
14	21.0	27.6	28.3	33.3	33.0	24.2	28.2	32.9	22.5	21.6
15	13.1	13.5	14.7	21.5	21.3	18.0	20.9	21.0	14.97	33.5
16	-	170.7	-	-	-	170.1	-	171.3	-	-
17	-	21.2	-	-	-	21.3	-	21.7	-	-
18	-	-	-	-	-	56.6	-	-	-	-
19	-	-	-	-	-	54.9	-	-	-	-
Ref.	Opiyo 2011	Wube et al., 2005	Chen et al., 2016	Opiyo, 2011	Xu et al., 2009b	Harinante-naina ET al., 2008	Aranda et al., 2001	Aranda et al., 2001	Opiyo et al., 2011	Montagnac et al.,1996

Table 3 Continued

C	**131^{C}**	**132^{B}**	**133^{B}**	**134^{C}**	**135^{M}**	**136^{M}**	**137^{C}**	**138**	**139^{C}**	**140^{P}**
1	34.9	34.8	34.5	34.6	71.3	73.6	34.9	34.9	34.0	42.4
2	18.0	18.7	18.5	18.2	26.2	22.0	18.3	18.5^{a}	17.9	17.8
3	41.1	41.9	41.5	41.4	34.5	35.0	41.5	42.3	41.3	35.9
4	33.1	33.1	32.6	32.9	33.2	32.9	33.3	33.4	32.7	34.7
5	51.3	46.5	45.5	46.1	44.2	45.4	51.8	52.8	51.6	49.2
6	27.3	28.0	27.9	27.9	17.7	17.9	17.7	25.7	17.5	71.0
7	65.0	60.6	59.9	59.7	21.4	22.0	21.9	18.7^{a}	23.7	68.8
8	128.0	128.0	129.4	127.9	130.6	132.0	140.7	136.1	157.9	156.9
9	170.1	168.2	168.5	171.1	166.3	162.9	150.8	159.5	138.3	135.7
10	37.7	37.2	37.8	37.3	43.4	42.0	36.3	35.3	34.5	33.6
11	97.6	102.4	101.0	98.0	99.9	90.8	170.6	172.2	169.2	171.6
12	171.0	170.7	170.1	172.1	171.7	170.5	169.9	71.0	96.2	69.3
13	33.3	33.4	32.9	33.1	21.4	21.7	33.4	33.8	33.0	20.0
14	21.5	21.6	21.3	21.5	33.1	33.5	21.4	21.8	20.9	32.7
15	19.3	18.0	20.0	17.5	21.4	20.6	20.7	20.5	19.7	27.7
16	-	66.0	65.5	-	-	169.6	-	-	-	-
17	-	15.3	17.1	-	-	21.5	-	-	-	-
18	-	-	-	-	-	169.9	-	-	-	-
19	-	--	-	-	-	21.5	-	-	-	-
Ref.	Sultana et al., 2011	Sakio et al., 2001	Sakio et al., 2001	Sultana et al., 2011	Aranda et al., 2001	Aranda et al., 2001	Sultana et al., 2011	Vlad et al., 2000	Montagnac et al.,1996	Opiyo, 2011

Table 3 Continued

C	141^C	142^C	143^C	144^M	145^M	146^M	147^M	148^M	149^M	150^M	151^C
1	33.1	36.3	35.0	36.2	69.4	71.5	70.0	71.8	70.9	48.2	39.6
2	20.8	20.6	22.0	119.8	122.6	118.9	123.6	119.2	119.5	64.8	18.6
3	43.1	43.0	42.5	138.7	143.0	144.6	143.0	144.0	144.0	51.0	42.3
4	35.4	35.4	33.7	34.6	35.1	35.0	35.9	35.2	35.2	34.6	33.3
5	49.3	50.6	47.0	48.2	41.3	42.2	42.5	42.7	42.7	52.7	53.2
6	69.8	69.6	61.9	18.9	18.8	18.8	20.0	18.6	18.7	130.4	22.6
7	73.8	66.6	70.3	21.5	21.2	21.3	22.0	21.3	21.7	129.4	23.3
8	154.5	150.6	160.6	124.1	125.9	126.7	131.0	130.6	132.6	79.0	114.3
9	137.9	140.3	136.4	168.5	167.6	165.4	166.9	163.3	161.2	70.2	64.5
10	36.5	33.3	35.8	35.5	41.3	39.7	43.0	40.0	40.5	40.9	37.1
11	172.1	171.0	172.4	68.3	69.2	68.5	99.2	97.3	91.0	101.7	98.3
12	66.1	70.2	172.4	174.1	174.7	174.0	173.6	171.5	170.6	80.9	134.6
13	33.4	33.2	39.2	22.2	21.8	22.0	22.4	22.2	21.9	23.0	33.7
14	23.1	22.9	29.3	32.7	31.4	31.2	31.5	31.3	31.4	33.4	21.8
15	18.4	18.3	19.1	20.6	20.9	21.1	19.6	19.5	20.6	15.8	14.0
16	170.9	171.1	-	-	-	170.5	-	171.6	169.5	-	172.9
17	21.4	21.3	-	-	-	21.6	-	21.3	169.8	-	30.3
18	-	169.8	-	-	-	-	-	-	21.3	-	14.1
19	-	20.8	-	-	-	-	-	-	21.3	-	-
Ref.	Mahmoud et al., 1980	Opiyo et al., 2011	Mahmoud et al., 1980	Aranda et al., 2001	Aranda et al., 2001	Aranda et al., 2001	Aranda et al., 2001	Aranda et al., 2001	Aranda et al., 2001	Kuang et al., 2016	Gaspar et al., 2008

Table 3 Continued

C	**152^{M}**	**153^{C}**	**154^{D}**	**155^{D}**	**156^{A}**	**157^{M}**	**158^{B}**	**159^{C}**	**160^{C}**	**161^{C}**	**162^{C}**
1	49.8	37.2	30.8	29.7	40.0	40.4	41.1	39.7	32.4	31.0	33.7
2	64.7	18.2	24.6	25.0	19.3	18.1	18.0	32.3	31.7	32.2	31.8
3	51.9	42.3	73.9	73.9	43.2	42.0	41.6	38.8	38.5	38.3	38.5
4	35.1	33.1	37.0	37.0	33.9	32.9	32.6	151.6	152.2	130.5	152.0
5	44.9	55.5	47.9	47.3	56.6	51.4	51.2	45.9	39.9	40.2	44.2
6	23.7	21.2	17.0	20.4	22.3	18.4	18.0	26.9	27.3	27.5	31.5
7	59.6	28.7	33.9	27.8	29.0	22.4	32.0	135.5	139.8	141.4	62.3
8	65.2	38.3	77.6	37.8	40.4	37.4	76.0	127.0	129.9	130.5	156.9
9	62.3	57.4	58.1	56.0	66.3	49.9	65.0	49.3	76.9	76.5	137.4
10	36.0	35.7	35.2	35.0	35.5	35.4	37.2	36.7	40.6	53.7	36.8
11	100.1	175.8	174.8	175.7	99.2	67.6	100.0	67.9	75.0	98.6	172.1
12	68.0	71.2	75.8	70.6	71.4	179.1	174.0	170.2	169.6	167.3	69.9
13	23.4	33.5	16.4	15.3	34.1	14.5	33.4	105.5	105.7	105.9	104.7
14	33.3	21.2	21.6	21.6	21.8	22.0	21.8	18.6	15.9	18.5	18.1
15	16.2	15.5	29.1	29.1	15.6	33.5	16.4	12.5	18.5	15.2	16.4
Ref.	Kuang et al., 2016	Paul et al., 1997	He et al., 2015	He et al., 2015	Montegnac et al., 1996	Aranda et al., 2001	Sakio et al., 2001	Wube et al., 2005	Mashimbye et al., 1999	Rajab and Ndegwa, 2000	Wube et al., 2005

Table 3 Continued

C	**163^c**	**164^c**	**165^c**	**166^c**	**167^c**	**168^c**	**169^c**	**170^c**	**171^c**	**172^c**
1	39.5	36.2	39.6	39.8	37.8	37.1	42.4	42.6	38.7	36.9
2	19.0	18.6	18.4	18.7	18.4	18.7	18.6	18.6	18.3	18.2
3	42.1	42.4	42.3	42.1	42.7	42.7	42.7	42.6	41.9	42.0
4	33.6	33.5	33.5	33.7	33.1	33.0	33.0	33.1	33.0	33.0
5	54.2	44.0	56.1	54.8	46.5	44.5	54.4	54.4	53.3	45.2
6	23.6	23.1	17.2	20.9	17.4	21.3	20.7	18.4	19.9	20.0
7	41.9	37.3	35.4	36.8	30.5	30.4	43.0	41.3	40.0	35.5
8	212.6	216.2	72.9	72.2	75.1	69.0	71.1	71.0	74.0	72.6
9	58.0	58.7	48.9	52.8	49.1	49.0	59.8	57.1	86.9	84.1
10	41.5	39.1	37.5	37.7	36.5	37.7	35.0	34.7	39.4	39.0
11	6.9	13.1	11.7	10.0	14.8	6.7	-	-	-	-
12	-	-	-	-	-	-	29.1	33.1	22.2	27.0
13	33.5	33.5	33.7	33.6	33.6	33.4	33.2	33.3	32.2	33.0
14	21.8	22.0	21.8	21.8	22.0	21.7	21.2	21.4	21.6	21.7
15	13.9	22.1	15.2	13.6	23.7	22.3	20.9	20.9	13.7	20.4
Ref.	Ohloff and Giersch, 1985	Ohloff and Giersch, 1985	Ohloff and Giersch, 1985	Ohloff and Giersch, 1985	Ohloff and Giersch, 1985	Ohloff and Giersch, 1985	Wahlberg et al., 1981	Wahlberg et al., 1981	Wahlberg et al., 1981	Wahlberg et al., 1981

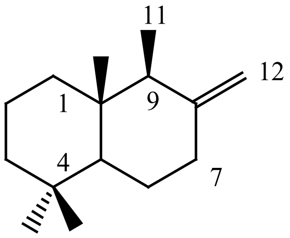
Table 3 Continued

C	**173^{C}**	**174^{C}**	**175^{C}**	**176^{C}**	**177^{C}**	**178^{C}**	**179^{C}**	**180^{C}**	**181^{C}**	**182^{C}**	**183^{D}**
1	38.4	38.0	38.3	38.0	22.0	36.3	20.0	33.2	32.6	32.8	33.6
2	18.6	18.5	18.1	18.5	32.7	21.2	34.4	18.2	17.9	18.1	18.1
3	41.2	41.5	40.8	41.1	41.4	39.9	41.0	41.6	41.4	41.5	42.2
4	32.8	33.0	33.0	32.9	33.2	34.5	34.9	33.6	33.7	33.6	32.3
5	50.6	48.6	50.4	50.3	39.0	41.5	36.4	49.4	48.4	49.0	40.1
6	35.4	27.0	34.0	35.6	17.8	18.2	18.3	24.4	25.2	24.2	22.9
7	201.6	67.7	200.8	202.3	208.2	71.5	207.5	143.4	156.2	145.1	140.8
8	131.2	139.1	137.7	133.9	56.2	58.9	60.3	132.9	189.9	135.8	132.2
9	158.3	164.5	163.1	158.9	59.5	70.7	71.5	205.9	203.4	206.7	71.4
10	36.9	37.7	38.3	18.3	46.1	33.0	41.1	45.1	45.3	45.2	36.9
11	-	-	-	-	-	-	-	-	-	-	-
12	15.5	196.2	193.8	61.4	16.8	18.2	15.5	16.4	189.9	62.4	168.0
13	32.2	32.7	32.4	32.2	22.5	25.0	33.7	32.3	32.2	32.3	32.6
14	20.9	21.3	21.0	20.9	32.6	32.5	32.1	22.2	22.1	22.2	21.4
15	18.5	20.1	18.1	36.7	16.9	19.5	17.0	17.2	16.8	17.1	18.4
16	-	-	-	-	-	170.4	-	-	-	-	-
17	-	-	-	-	-	21.1	-	-	-	-	-
Ref	Cuellar et al., 2003	Fukuyama et al.,1985	Bastos et al., 1999	Cuellar et al., 2003	Cuellar et al., 2003	Montenegro et al., 2013	Montenegro et al., 2014	Cuellar et al., 2003	Cuellar et al., 2003	Cuellar et al., 2003	Liu et al., 2010

*Solvent are indicated by superscripts A (Acetone-d6), B (C6D6), C (CDCl3), D (DMSO-d6), DC (CD2Cl2), P (C5D5N), M (CD5OD). a, b, c within a vertical column may be reversed.

Table 4

Structures of drimanes **25-34.**



25 Drim-8(12)-ene

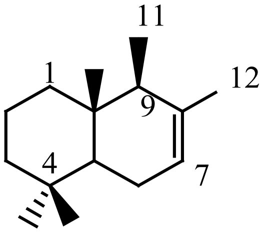
26 $\Delta^{9(11)}$	**29** 3β-OAc, 11-OH	**32** 3β OH, 11-OAc
27 11-OH, albicanol	**30** 11-OAc, albicanylacetate	**33** 3β, 11-OAc
28 7α, 11-OH	**31** 7α-OH, 11-OAc	**34** 3β-OAc, 11- CO_2Me

2.3. Drim-7-ene sesquiterpenes

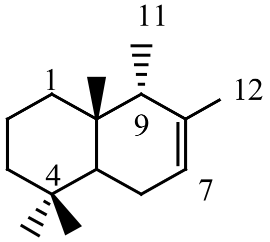
^{13}C NMR data of several drim-7-enes have been reported and compounds **35-80** (Table 5) are some of the most important examples (Panasenko et al., 2004; Lu et al., 2009; Xu et al., 2009a; Dacunto, 2012; Yonemura et al., 2012; Derita et al., 2013; Zhao et al., 2014; Xiao et al., 2017; Santoso et al., 2018). Hydroxylation is mostly observed at C-11, C-9, C-6 (Aasen et al.,1977; Barrero et al.,1995; Grabley et al.,1996 Chaudhary et al., 2008; Lu et al., 2009; He et al., 2014; Xiao et al., 2017). Drim-7-ene derivatives having the hydroxyl group at C-3 include compounds **38**, **47**, **50**, **51**, **55**, **57-58**, **61** and **62**. In such compounds, the oxymethine C-3 carbon resonates between δ 78.9 and 79.7 ppm (Lu et al., 2009; Xu et al., 2009a; Dacunto, 2012; He et al., 2014; Zhao et al., 2014). Drim-7-ene derivatives having hydroxyl group at C-9 include **42-45**, **47**, **48**, **70-72** and the oxygenated C-9 carbon resonates between δ 74.4-76.6 ppm (Lagnel et al., 2000; Panasenko et al., 2004; Lu et al., 2009). Drim-7-ene derivatives having hydroxyl group at C-6 such as **43**, **44**, **67** and **71** have also been reported and their oxymethine C-6 carbon resonates between δ 65.4-68.4 ppm (Lagnel et al., 2000). The dial derivatives **59-64** (Aasen et al., 1977; Rodriguez et al., 2005; Dacunto, 2012) and mono-al derivatives **41**, **65**, **69** and **74** are known (Fukuyama et al.1985; Jansen, 1993; Liu et al., 2010; Derita et al., 2013). The carbonyl carbons peaks appear between δ 201.3 -203.9 and 192.3-193.9 ppm for C-11 and C-12 carbonyl carbons, respectively (Kioy et al., 1989; Rodriguez et al., 2005; Dacunto, 2012; Santoso et al., 2018). Changweikangic acid B (**65**), a drim-7-ene derivative with COOH substitution at C-12 had the carbonyl carbon resonating at δ 167.5 ppm (Liu et al., 2010), while polygonic acid (**74**) with COOH substitution at C-11 had the carbonyl carbon peak at δ 176.6 ppm (Fukuyama et al.,1985). Compound 65 was isolated from a mixture of *Daphniphyllum calycinum* and *Polygonum hydropiper*. Acetylated derivatives **49-51**, **57**, **58**, **63**, **68**, **73** and **80** have been reported with acetylation mainly occurring at C-11 (Mahmoud et al., 1980; Ramirez et al., 1993; Barrero et al., 1995; Lagnel et al., 2000; Rodriguez et al., 2005; He et al., 2014).

Table 5

Structures of drimanes **35-80.**



40 Drim-7-ene



For cpds 36, 54, 63 & 64

35 11- OH, drimenol	**51** 3β-OH, 11- $OCOCH_2OH$	**66** 9α-OH, 11, 12-CHO, warburganal
36 11- OH, isodrimenol	**52** 11, 12-OH, polygodiol	**67** 6α 9α-OH, 11, 12-CHO, mukaadial
37 3-oxo, 11- OH	**53** 2α, 11, 12-OH, pestalotiophol A	**68** 6β-OAc, 9α-OH, 11, 12-CHO, ugandensidial
38 3β,11-OH	**54** 11, 12-OH, isodrimenediol	**69** $\Delta^{9(11)}$, 12-CHO
39 6-oxo, 11- OH	**55** 3β, 11, 12-OH, sulphureuine H	**70** 9α, 11,12-OH
41 11- CHO, drimenal	**56** 3oxo, 11, 12-OH	**71** 6β-9α, 11, 12-OH,
42 9α,11-OH	**57** 3β, 12-OH, 11-OAc, phellinuin F	**72** 6β-OMe, 9α, 11, 12-OH, ustusol C
43 6α, 9α, 11-OH, albrassitriol	**58** 3β, 11-OH, 12-OAc, phellinuin G	**73** 11- OAc, 12- OH
44 6 β, 9α, 11-OH, 6-epi-albrassitriol	**59** 11, 12-CHO, polygodial	**74** 11-COOH, 12-CHO, polygonic acid
45 6-oxo, 9α, 11-OH	**60** 1β-OH, 11, 12-CHO	**75** 3β, 11, 12, 14-OH, phellinuin A
46 6-oxo, $\Delta^{9(11)}$	**61** 3β-OH, 11, 12-CHO	**76** 3β, 12, 14-OH, 11-OAc, phellinuin C
47 6-oxo, 3β, 9α, 11-OH, ustusol A	**62** 3β-OAc, 11, 12-CHO	**77** 3β, 11, 14-OH, 12-OAc, phellinuin D
48 6-oxo, 2β, 9α, 11-OH, ustusol B	**63** 11, 12-CHO, isopolygodial	**78** 11, 12, 13-OH
49 6-oxo, 11- OAc	**64** 1β-OH, 11, 12-CHO	**79** 3β, 11, 12, 13-OH, phellinuin B
50 3β-OH, 11- OAc	**65** 11- CHO, 12-COOH, changweikangic acid B	**80** 3β, 12, 13-OH, 11-OAc, phellinuin E

In drim-7-enes with no substitution in close proximity to the double bond, e.g. in drimane **40**, the C-7 and C-8 olefinic carbons resonate at δ 121.9 and 135.3 ppm, respectively (Yonemura et al., 2012). The presence of aldehyde functional group at C-11 in drimane **41** leads to downfield (~3.4 ppm) and upfield (~4.5 ppm) shifts for the olefinic C-7 and C-8, respectively. The presence of two aldehyde groups, at C-11 and C-12, leads to downfield shifts of ~32.5 and ~2.8 ppm for the olefinic C-7 and C-8, respectively (cf. drimanes **40** and **59**, Table 3). The presence of hydroxyl group at C-11 deshields C-7 by 2.0 ppm and shields C-8 by 1.9 ppm. It also leads to downfield (+49.7 ppm) and upfield (-5.0 ppm) shifts for C-11 and C-9, respectively (cf. drimanes **35** and **40**). In drim-7-enes such as **42** that have two hydroxyl groups (at C-9 and C-11), the olefinic C-7 and C-8 carbons resonate at ~127 and 135 ppm, respectively (Barrero et al., 1999). The presence of hydroxyl group at C-3 in drim-7-enes such as in compound **38** deshields C-3 and C-2 by ~37 ppm and ~9 ppm, respectively, while C-1 is shielded by 0.5 ppm. The 3-oxo derivatives of drim-7-ene including 3-oxodrim-7-ene-11-ol (**37**) and 3-oxodrim-7-ene-11, 12-diol (**56**) were reported having C-3 carbonyl carbon resonating at δ 215.1-216.7 (Xu et al., 2009a; Zhao et al., 2014)]. The 6-oxo derivatives of drim-7-ene such as **39** and **45**-

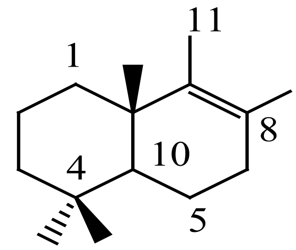
40 have the carbonyl carbon resonating at ~200 ppm (Lagnel et al., 2000; Panasenko et al., 2004; Lu et al., 2009). The presence of the oxo group at C-6 deshields C-7 by ~6 and C-8 by ~22 ppm, thus the olefinic carbons resonate at about δ 129 and 156 ppm, respectively. Drim-7-enes such as **37** and **56** that have oxo group at C-3 are deshielded at C-3 and C-2 but shielded at C-1 by about 174, 20 and 5 ppm, respectively. Drimenol (**35**), isodrimenol (**36**), polygodiol (**52**), isodrimenediol (**54**), polygodial (**59**) and isopolygodial (**63**) are sets on epimers at the C-9 stereogenic center. The configuration of their C-11 substituent is evidenced by the noticeable difference in the chemical shifts of the C-1, C-5 and C-15γ carbons (Rodriguez et al 2005). For example, in polygodial (**59**) and isopolygodial (**63**), the difference in the chemical shifts of the C-1, C-5 and C-15γ carbons is observed [Δδ = δ (**59**) - δ(**63**): +2.4, +4.8 and -6.3 ppm, respectively].

2.4. Drim-8(9)-ene sesquiterpenes

Drimane derivatives **81-93** (Table 6) having a double at 8:9 have been reported by several workers, showing C-8 and C-9 olefinic carbons resonating between δ 124.3-134.9 and 136.2-169.5 ppm, respectively (Benites et al., 2001; Kuchkova et al., 2005). Drim-8(9)-enes with no substituent in close proximity to the double bond, e.g. **81** have the olefinic C-7 and C-8 resonating at ~124 and ~136 ppm, respectively (Yonemura et al., 2012). Compounds **83-87** and **93** have hydroxyl group at C-11 and the oxymethylene carbon resonates between δ 57.7-58.5 ppm (Benites et al., 2001; Panasenko et al., 2004; Kuchkova et al., 2005). Compounds **85-87** have hydroxyl group at C-12 and the oxymethylene carbon resonates between δ 56.5 - 64.0 ppm (Benites et al., 2001; Kuchkova et al., 2005).

Table 6

Structures of drimanes **81-93.**



81 Drim-8(9)-ene

82 7-oxo	**86** 7β, 11, 12-OH	**90** 7β-OH, 11-OAc
83 11-OH	**87** 11, 12-OH	**91** 7β-OH, 11, 12-OAc
84 7-oxo, 11-OH	**88** 11-OAc	**92** 6-OAc, 11-CHO
85 7-oxo, 11, 12-OH	**89** 7-oxo, 11-OAc	**93** 6-OAc, 11-OH

The presence of hydroxyl group at C-11 deshields the olefinic carbons C-8 and C-9 by ~8 ppm and ~6 ppm, respectively. For example, in drim-8(9)-en-11-ol (**83**), C-8 and C-9 carbons resonate at δ 132.5 and 141.1 ppm, respectively (Kuchkova et al., 2005). In drim-8(9)-enes having two hydroxyl groups (at C-11 and C-12), the olefinic carbons are less shielded and a downfield shift of ~12 ppm and ~10 ppm are observed for C-8 and C-9, respectively. For example, in 11,12-dihydroxydrim-8-ene (**87**) the olefinic carbons C-8 and C-9 resonate at δ 136.0 and 146.2 ppm, respectively (Benites et al., 2001). Monoacetyl derivatives **88-90**, **92**, **93** and diacetyl derivatives such as **91** were also reported (Barrero et al., 1995; Lagnel et al., 2000; Panasenko et al., 2004). Acetylation of the hydroxyl group at C-11 further deshields C-8 but shields C-9 by ~2.8 and ~5.6 ppm. In 11-acetoxy-8-drimene (**88**), the olefinic carbons C-8 and C-9 resonate at δ 135.3 and 135.5 ppm, respectively, while in 11-acetoxy-8-drimen-7β-ol (**90**), they resonate at 136.8 and 138.7 ppm, respectively (Barrero et al., 1999). The 7-oxo derivatives of drim-8(9)-ene such as **82**, **84**, **85** and **89** have the C-7 resonating at δ 199-202 ppm (Benites et al., 2001; Kuchkova et al., 2005). The presence of oxo group at C-7 deshields the olefinic carbons C-8 and C-9 by ~5-10 and ~22-44 ppm, respectively, making the olefinic carbon to resonate between δ 129-137 and 158-170 ppm, respectively. In drim-8-en-7-one (**83**), C-7, C-8, and C-9 resonate at δ 199.9, 129.3 and 165.3, respectively (Panasenko et al., 2004).

2.5. 8α, 9α and 7α, 8α-Epoxydrimane sesquiterpenes

^{13}C NMR chemical shifts of synthetic 8α,9α-epoxydrimanes (Table 7) have been reported by several groups of workers. The ^{13}C values of some representatives **94-98** are shown in Table 3. The oxygenated carbons C-8 and C-9 resonate between δ 64.8-66.5 and 69.6-73.2 ppm, respectively (Lagnel et al., 2000; Benites et al., 2001; Panasenko et al., 2004). In 7-oxo-8α,9α-epoxydrimanes derivative, e.g. 11-hydroxy-8α,9α-epoxydriman-7-one

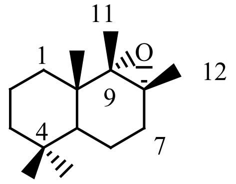
(97), C-7, C-8 and C-9 resonate at δ 207.7, 66.5 and 65.5 ppm, respectively (Barrero et al., 1999). Hydroxylated derivatives **95-98** having the hydroxyl group mostly at C-7, C-11 and C-12 have been reported (Barrero et al., 1999; Lagnel et al., 2000; Benites et al., 2001; Panasenko et al., 2004). In the synthetic 7α, 8α-epoxydrimane derivatives, e.g. **99-101**, the C-7 and C-8 oxygenated carbons resonate at δ 60.7 and 65.2 ppm (De Bernardi et al., 1980; Lagnel et al., 2000). The 6-oxo derivatives (**99** and **100**) had the C-6 carbon resonate between δ 204.5 and 205.0 ppm (De Bernardi et al., 1980; Lagnel et al., 2000).

2.6. Drim-6,8-diene and drim-5,8-diene sesquiterpenes

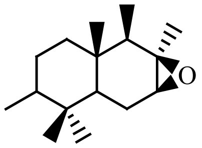
^{13}C signals of drim-6,8-diene and drim-5,8-diene sesquiterpenes such as **102-103** and **104-105**, respectively (Table 7) were reported. In drim-6,8-dien-11-al (**102**) and 7,11-diacetoxydrima-6,8-diene (**103**), the olefinic carbons C-6, C-7, C-8 and C-9 resonate at δ 136.5, 130.2, 144.2, 142.9 and at 115.6, 129.0, 139.7 and 146.8 ppm, respectively (Lagnel et al., 2000; Vlad et al., 2006). In 6-oxodrim-5,8-diene derivatives **104** and **105**, the olefinic carbons C-5, C-9, C-8 and C-6 resonated between δ 172.6-173.1, 154.7-160.4, 135.2-133.3 and 123.9-124.1 ppm, respectively, while the C-7 carbonyl carbon in the compounds resonated between δ 186.9-185.3 ppm (Vlad et al., 2006).

Table 7

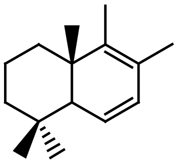
Structures of drimanes **94-105.**



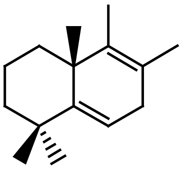
94-98



99-101



102-103



104-105

94 7-oxo	**98** 6α-OAc, 11-OH	**102** 11- CHO
95 7β-OH	**99** 6-oxo, 11-OH, uvidin A	**103** 7, 11-OAc
96 11, 12-OH	**100** 3β, 11-OH, 6-oxo, uvidin B	**104** 7-oxo, 11-OAc
97 7-oxo, 11-OH	**101** 6β, 11-OH, uvidin C	**105** 7-oxo, 11, 12-OAc

2.7. Rearranged drimane sesquiterpenes

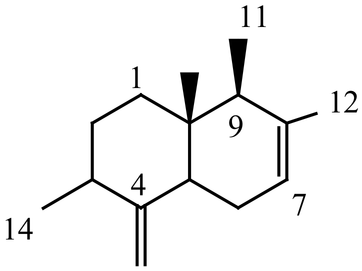
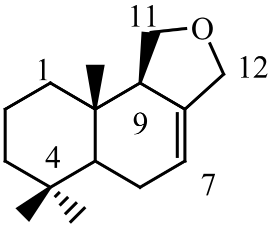
Assignment of ^{13}C signals of a number of rearranged drimane sesquiterpenes, e.g. **106-109** (Table 8) have been reported (Wube et al., 2005; Opiyo, 2011; He et al., 2015). Sulphureine D (**106**), muzigadial (**107**), 9-deoxymuzigadial (108) and 6α-hydroxymuzigadial (**109**) have an exocyclic double bond at C-4 and a methyl group at C-3. The olefinic carbons C-4 and C-13 resonate between δ 149.1-155.6 and 106.0 -106.9 ppm, respectively (Wube et al., 2005; He et al., 2015). In 106, the hydroxylated carbons C-11 and C-12 resonate at δ 60.7 and 65.0 ppm, respectively (Table 3). In drim-4(13)-ene derivatives **107-109** which have additional double bond at 7:8, olefinic carbons C-7 and C-8 resonate between δ 150.8-153.8 and 139.6-139.3 ppm, respectively (Mashimbye et al., 1999; Wube et al., 2005).

2.8. Tricyclic drim-7-ene sesquiterpenes

^{13}C NMR assignments of some tricyclic drim-7-enes **110-126** (Table 8) are shown in Table 3 (Wube et al., 2005; Shiono et al., 2007; Harinantenaina et al., 2008; Xu et al., 2009b; Opiyo, 2011; Derita et al., 2013; Chen et al., 2016; Kuang et al., 2016). In dehydroxydrimeninol (**110**), the olefinic carbons C-7 and C-8 resonate at δ 127.4 and 136.9 ppm, respectively, while the oxymethylene carbons C-11 and C-12 resonate at δ 61.4 and 67.4 ppm, respectively (Derita et al., 2013). The presence of hydroxyl group at C-11 deshields C-11 (~38 ppm) and C-12 (~ 1.5 ppm) but shields C-7 (~ 10 ppm) and C-8 (~0.4 ppm). For example, in isodrimeninol (**114**), C-7, C-8, C-11 and C-12 resonate at δ 117.1, 136.5, 99.4 and 68.9 ppm, respectively (Derita et al., 2013). The lactone carbonyl carbon of 11,12 olides such as compounds **111**, **112**, **117** and **118** resonates between δ **175-178** ppm (Shiono et al., 2007; Rukachaisirikulet al., 2010; Kuang et al., 2016). The presence C-11 ester group, e.g. drimenin (**111**) shields the C-7 and C-8 olefinic carbons by 6.2 and 7.0 ppm, respectively but deshields the oxymethylene C-12 carbon by 2.4 ppm. In compound **111**, C-7, C-8 and C-12 ^{13}C peaks were observed at δ 121.2, 129.9 and 69.8 ppm, respectively (Rukachaisirikul et al., 2010). In 12,11 olides such as compounds **121-123**, the carbonyl carbon resonates more upfield between δ 167-171 ppm as a result of conjugation. The presence of C-12 ester group, as in cinnamolide (**121**), deshields the olefinic C-7 carbon by 8.5 ppm but shields C-8 by 9.9 ppm. In drimanes such as **124-126**, the oxygenated quaternary C-9 carbon resonates between δ 75.7-77.3 ppm (Harinantenaina et al., 2008; Xu et al., 2009b; Opiyo, 2011). The presence of

Table 8

Structures of drimanes **106-126.**

 106-109	 110-126
106 3β-H, 8α, 11, 12-OH, sulphureuine D	**117** 6β, 9α-OH, 11-oxo, stobilactone A
107 3α-H, 9α-OH, 11, 12-CHO, muzigadial	**118** 2α, 6β, 9α-OH, 11-oxo, stobilactone B
108 3α-H, 11, 12-CHO, 9-deoxymuzigadial	**119** 3α, 9α, 11α –OH
109 3α-H, 6α, 9α-OH, 11, 12-CHO	**120** 3α, 6β, 9α, 11α-OH
110 dehydroxydrimeninol	**121** 12-oxo, cinnamolide
111 11-oxo, drimenin	**122** 3β- OAc, 12-oxo
112 3α-OH 11-oxo	**123** 3β, 11α-OH, 12-oxo, hydroxydendocarbin A
113 3β, 11α-OH, danilol	**124** 9α-OH, 12-oxo
114 11α-OH, isodrimeninol	**125** 9α, 11α-OH, 12-oxo, ugandenial A
115 11α, 14-OH	**126** 6β-OAc, 9α-OH, 11α, 12β-OMe
116 2α, 11α-OH	

the hydroxyl group at C-9 deshields C-7, C-8, C-9 and C-11 but shields C-12. For example, in 9α-hydroxycinnamolide (**124**), C-7, C-8, C-9 and C-11 resonate at δ 141.1 (+5.2), 130.0 (+2.8), 77.3 (+10.4) and 74.3 (+7.4) ppm, respectively. Compounds **124** and **125** were isolated form *Warburgia ugandensis* Engl. (Opiyo, 2011; Xu et al., 2009b), while cinnamodial 11α, 12β-dimethyl acetal (126) was isolated form *Cinnamosma madagascariensis* Danguy (Harinantenaina et al., 2008).

2.9. Tricyclic drim-8(9)-ene lactone derivatives

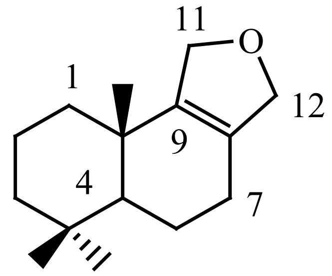
In tricyclic drim-8(9)-ene sesquiterpenes such as **127-143** (Table 9), the lactone carbonyl carbon resonates between δ 164.9-172.4 ppm, while the olefinic carbons C-8 and C-9 resonate between δ 122.3-140.7 and 150.8 -171.7 ppm, respectively (Aranda et al.,1992; Montagnac et al., 1996; Sakio et al., 2001; Opiyo et al., 2011; Sultana et al., 2011). In drim-8(9)-ene lactones with no substituent in close proximity to the lactone ring, e.g. 3β-hydroxyconfertifolin (**127**), the olefinic carbons C-8 and C-9 resonate at δ 123.8 and 170.0, ppm respectively. Bemadienolide (**129**) has an additional double bond at C-6 evidenced by chemical shifts at δ 117.6 and 131.7 ppm for C-6 and C-7, respectively (Kioy et al., 1990; Opiyo et al., 2011). The presence of additional double bond shielded C-8 (1.5 ppm), C-11 (0.5 ppm), C-12 (4.5) but shielded C-9 (1.7 ppm) in compound 129 (Table 3). Compounds **130-132**, **134** and **135**, which have a hydroxyl group at C-11 showed the oxygenated C-11 carbon peak between δ 96.8-99.9 ppm which is equivalent to a downfield shift of ~33 ppm. The presence of hydroxyl group at C-11 deshields C-8 but shields C-9 and C-12. For example, in 11β-hydroxyconfertifolin (**130**), C-8, C-9 and C-12 peaks were observed at δ 128.3, 167.7 and 172.0 ppm, respectively (Montagnac et al., 1996). Compounds **131-134** have hydroxyl group at C-7 and the oxymethine carbon resonates between δ59.7-65.0 ppm which is more downfield by ~43 ppm. In dihydroxyconfertifolin (**136**) and diacetoxyconfertifolin (**136**), C-8, C-9, C-11 and C-12 carbons resonate at δ 130.6, 166.3, 99.9, 171.7 and 132.0, 162.9, 90.8, 170.5 ppm, respectively (Aranda et al., 2001). Winterin (**137**) was isolated from Polygonum hydropiper (Linn.) and its C-8, C-9, C-11 and C-12 carbons resonate at δ 140.7, 150.8, 170.6 and 169.9 ppm, respectively (Sultana et al., 2011).

2.10. Tricyclic drim-2,8-diene lactone sesquiterpenes

Synthetic drimane 12,11 olides such as **144-149** (Table 9) having two double bonds at C-2 and C-8 have been reported (Table 3). Their lactone carbonyl carbon resonates between δ170.6-174.7 ppm, while the olefinic carbons resonate between δ 118.9-123.6, 138.7-144.6, 124.1-132.6 and 161.2-168.5 ppm for C-2, C-3, C-8 and C-9, respectively (Aranda et al., 1992). For non-substituted compounds in this series, e.g. 2,3-dehyddroconfertifolin (**144**), the olefinic carbons C-2, C-3, C-8 and C-9 resonate at δ 119.8, 138.7, 124.1 and 168.5 ppm, respectively. Presence of hydroxyl group at C-1 deshields C-1, C-2, C-3, C-8, C-11 and C-12 but shields C-9. For example, in 1α-hydroxy-2,3-dehyddroconfertifolin (**145**),C-1, C-2, C-3, C-8, C-9, C-11 and C-12 peaks were observed at δ 69.4 (+33.2), 122.6 (+2.8), 143.0 (+4.3), 125.9 (+1.8), 167.6 (-0.9) , 69.2 (+0.9) and 174.7 (+0.6) ppm, respectively (Aranda et al., 2001). In derivatives **146**, **148** and **149** having acetyl groups at C-1, the oxymethine carbon C-1 resonate between 70.9 -71.8 ppm (Aranda et al., 1992).

Table 9

Structures of drimanes **127-149.**



127-149

127 3β-OH	**139** 11-oxo, 12β-OH
128 1α- OAc, 11α-OH	**140** 6β, 7α-OH, 11-oxo, deacetoxyugandensolide
129 Δ^{6}, bemadienolide	**141** 6β-OAc, 7α-OH, 11-oxo, ugandensolide
130 11β-OH	**142** 6β-OAc, 7α- OAc, 11-oxo
131 7β, 11α-OH, 12-oxo, fuegin	**143** 7α-OH, 11-oxo, futronolide
132 7α-OH, 11β-OEt, 12-oxo, dendocarbin J	**144** 12-oxo, Δ^{2}
133 7α-OH, 11α-OEt, 12-oxo, dendocarbin K	**145** 1α-OH, 12-oxo, Δ^{2}
134 7α, 11β-OH, 12-oxo, dendocarbin L	**146** 1α-OAc, 12-oxo, Δ^{2}
135 1α, 11α-OH, 12-oxo	**147** 1α, 11α-OH, 12-oxo, Δ^{2}
136 1α, 11α-OAc, 12-oxo	**148** 1α-OAc, 11α -OH, 12-oxo, Δ^{2}
137 11, 12-oxo, winterin	**149** 1α, 11α -OAc, 12-oxo, Δ^{2}
138 11-oxo, sodrimenin	

2.11. Miscellaneous unsaturated tricyclic drimane sesquiterpenes

In 11,12-epoxy-2α,8α,11α-trihydroxydrim-6-ene (**150**) olefinic C-6 and C-7 carbon resonate at δ 130.4 and 129.4 ppm, respectively while the oxygenated carbon C-2, C-8, C-11 and C-12 peaks were observed at δ 64.8, 79.0, 101.7 and 80.9 ppm, respectively (Kuang et al., 2016). Drim-8(12)-ene 11,12-epoxide (**151**) showed the olefinic carbon peaks at δ 114.3 and 134.6 ppm acetal C-11 carbon peak δ 98.3 ppm (Gaspar et al., 2008). In 2α-hydroxy-7α,8α-epoxyisodrimeninol (**152**), the epoxide carbon peaks at δ 59.6 and 65.2 ppm for C-7 and C-8, respectively (Kuang et al., 2016). Compounds **151** and **152** were isolated from endophytic fungi (Kuang et al., 2016).

2.12. Saturated tricyclic drimane sesquiterpenes 153-158

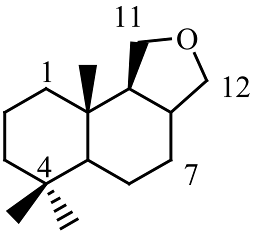
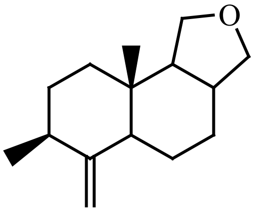
^{13}C NMR signals for dihydrodrimenin (**153**), sulphureuine E (**154**), sulphureuine F (**155**) and dihydroisodrimeninol (**156**) were reported (Table 3). In dihydrodrimenin (**153**), the lactone carbonyl C-11 carbon peak was observed at δ 175.8 ppm, while C-8 and C-12 peaks were at δ 38.3 and 71.2 ppm, respectively. In sulphureuine F (**155**), C-8, C-9, C-11 and C-12 signals were observed at δ 37.8, 56.0, 175.7 and 70.6 ppm, respectively. The presence of hydroxyl group at C-8 deshielded C-8, C-9, and C-12 but shielded C-11. For example, in sulphureuine E (**154**), C-8, C-9, C-11 and C-12 peaks were observed at 77.6 (+39.8), 58.1 (+2.1), 174.8 (-0.9) and 75.8 (+5.2) ppm, respectively. Drimanes **154** and **155** have hydroxyl group at C-3 and the oxymethine peak was observed at δ 73.9 ppm. Compounds **157** and **158** are drimane 12,11-lactone derivatives and their lactone carbonyl carbon resonated at δ 174.0-179.1 ppm (Table 3). Drimanes **153-156** were isolated from cultures of fungi.

2.13. Rearranged tricyclic drimane sesquiterpenes

Drim-4(13)-7-diene 12,11 olide derivatives **159-161** (Table 10) have been reported and their lactone carbonyl carbon resonates between δ 167.3-170.2 ppm (Mashimbye et al., 1999; Rajab and Ndegwa, 2000; Wube et al., 2005). In drim-4(13), 8-diene 11,12 olide derivative **162**, the carbonyl carbon peak was more downfield at δ 172.1 ppm. The olefinic carbons C-4, C-8, C-9 and C-13 resonate between δ 152.0, 156.9, 137.4 and 104.7 ppm, respectively (Table 3). Compounds **159**, **161** and **162** were isolated from Warburgia ugandensis Sprague, while compound **160** was isolated from *Warburgia salutaris* (Bertol. f.) Chiov.

Table 10

Structures of drimanes **150-162.**

 150-158	 159-162
150 2α, 8α, 12α-OH, Δ^6	157 12-oxo, confertifolin dihydro
151 12α-EtCOO, $\Delta^{8(12)}$	158 8α, 11α-OH, 12-oxo, dendocarbin D
152 7,8-epoxy, 2α, 12α-OH	159 12-oxo, Δ^7
153 11-oxo	160 9α-OH, 12-oxo, Δ^7, muzigadiolide
154 3α, 8β-OH, 11-oxo, sulphureuine E	161 9α, 11α -OH, 12-oxo, Δ^7,
155 3α-OH, 11-oxo, sulphureuine F	162 7β-OH, 11-oxo, $\Delta^{8(9)}$
156 11α-OH	

2.14. Nor-drimane sesquiterpenes

Compounds belonging to the nordrimane group have been identified in *Capsicodendron dinisii* (Schwacke) (Bastos et al., 1999), *Polygonum hydropiper* (Fukuyama et al., 1985) and certain tobacco varieties (Wahlberg et al., 1981). The compounds are partly responsible for the characteristic flavor in tobacco. Some examples of 12-nor (**163-168**) and 11-nor (**169-18**) **3** drimane derivatives are given in Table 11. Their chemical shifts are summarized in Table 3 (Wahlberg et al., 1981; Ohloff and Giersch, 1985; Bastos et al., 1999; Cuellar et al., 2003; Liu et al., 2010; Montenegro et al., 2014).

3. Concluding remarks

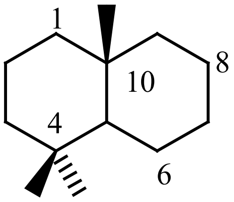
This review provides an extensive list of ^{13}C NMR spectral data of drimane sesquiterpenes that have been reported by various workers to-date. It has also provided a brief discussion on the substituent effect on the ^{13}C shielding of the drimane sesquiterpenes. It is evident that direct access to such data will simplify the structure elucidation of new related compounds by data comparison. However, further review of the compounds is still necessary to compile the ^{1}H NMR spectral data of the compounds.

Conflict of interest

The author declares that there is no conflict of interest.

Table 11

Structures of nordrimane **163-183.**

	
163 8-oxo, 11β -CH_3	**174** 7β-OH, 12-CHO, $\Delta^{8(9)}$, isopolygonal
164 8-oxo, 11α-CH_3	**175** 7-oxo, 12-CHO, $\Delta^{8(9)}$, polygonone
165 8β-OH, 11β -CH_3	**176** 7-oxo, 12-OH, $\Delta^{8(9)}$
166 8 α-OH, 11β -CH_3	**177** 7-oxo, 8β, 9β-epoxy, 12α-CH_3
167 8β-OH, 11α-CH_3	**178** 7β-OAc, 8α,9α- epoxy, 12β -CH_3
168 8α -OH, 11α-CH_3	**179** 7-oxo, 8α,9α- epoxy, 12β -CH_3
169 8α-OH, 12β -CH_3	**180** 9-oxo, 12 -CH_3, Δ^{7}
170 8β-OH, 12α-CH_3	**181** 9-oxo, 12-CHO, Δ^{7}
171 8α, 9β-OH, 12β -CH_3	**182** 9-oxo, 12-OH, Δ^{7}
172 8α, 9α-OH, 12β -CH_3	**183** 9α-OH, 12-COOH, changweikangic acid A
173 7-oxo, 12 -CH_3, $\Delta^{8(9)}$	

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