

# A View on Siloxanes and Other Silyl Substituted Compounds Isolated from Plants, Fungi, Bacteria and Other Organisms

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## Abstract

Often, siloxanes and silanes have been reported as constituents of plant extracts, where the authors have not remarked on whether the compounds are natural plant metabolites, xenobiotics stemming from anthropogenic environmental pollution or contaminants originating from the analysis itself. This contribution critically reviews and evaluates silyl containing compounds in plant extracts.

## Keywords

Natural Product Isolation, Silanes, Siloxanes, Xenobiotics

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## 1. Introduction

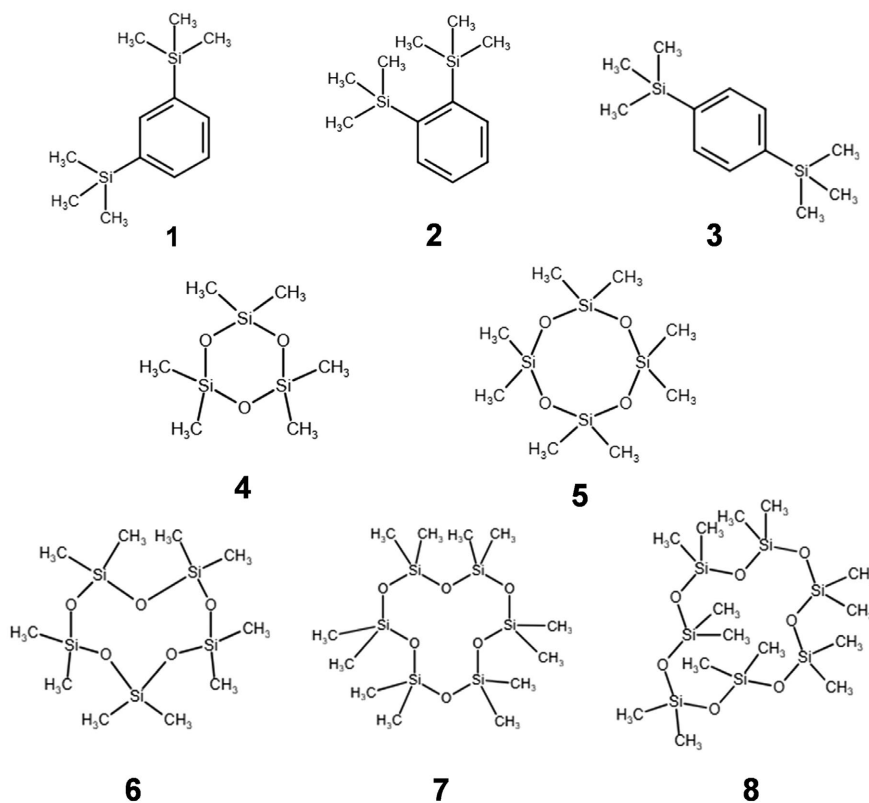
Natural products are chemical compounds produced by living organisms. When extracted from their natural sources, often, these compounds are present as complex mixtures, necessitating separation for accurate structural identification. The isolation of a natural product may involve obtaining sufficient quantities of a pure compound for derivatization, biological testing, and potentially for potential commercial use. Alternatively, it may refer to isolating only analytical quantities for the purpose of identification and quantification within biological tissues.

In the latter case, gas chromatography–mass spectrometry (GC/MS) is commonly employed. This technique allows for the screening of biological tissues and fluids for known compounds, supported by existing mass spectral databases. In contrast, the former scenario—particularly when novel compounds are involved—requires a broader range of analytical tools. These may include nuclear magnetic resonance (NMR) spectroscopic techniques, single-crystal X-ray diffraction, and elemental

analysis to complement mass spectrometry.

In recent years, extensive chemical profiling of essential oils of plants has been conducted, including going down to the level of distinguishing metabolites in essential oils of different phenotypes of the same species [1], often relying solely on GC/MS. This is especially prevalent when evaluating plant materials for potential health benefits or pharmaceutical properties. However, these studies frequently do not distinguish whether the detected compounds are endogenous metabolites or xenobiotics—foreign substances introduced into the organism.

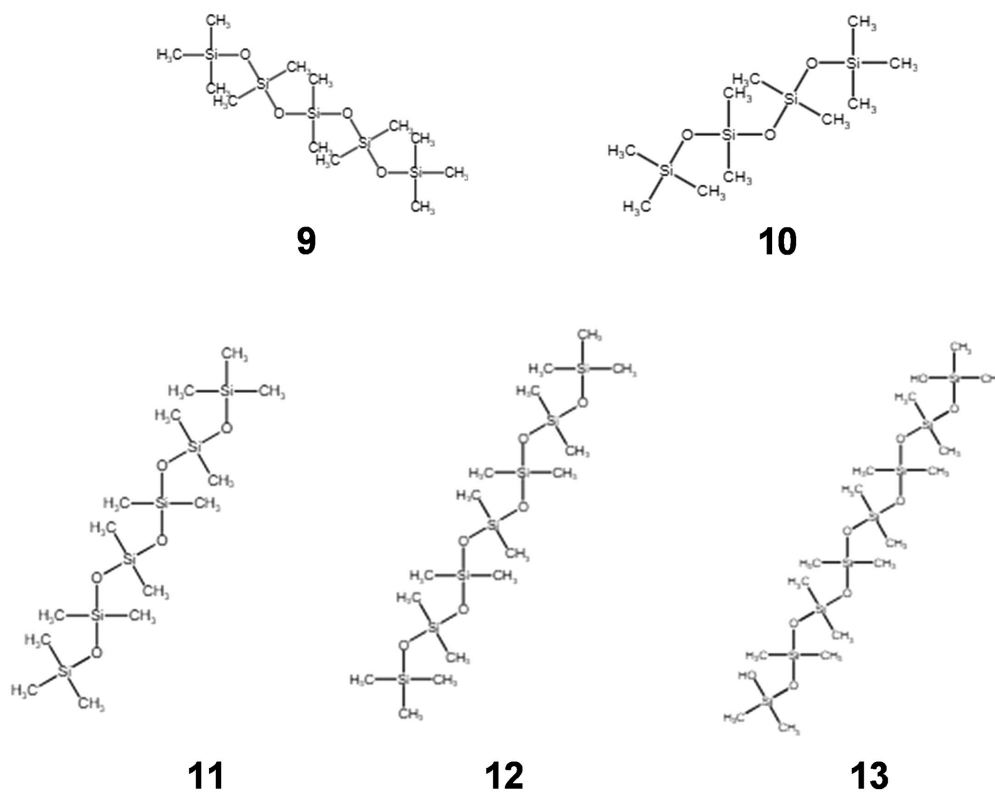
On the one hand, this lack of differentiation allows for an unbiased assessment of anthropogenic xenobiotics across ecosystems and can supplement targeted environmental monitoring efforts. On the other hand, it would be helpful, if specific constituents are realized as xenobiotics rather than metabolites of the plant early on, so that, if xenobiotics, they may be disregarded as contributing to potential health effects of extracts in general of that particular plant species. A notable example is the isolation of phthalates from numerous plant species, reported as natural constituents without clarification of their likely anthropogenic origin [2] in most cases [3].



**Figure 1.** Bis(trimethylsilyl)benzenes **1-3** and cyclic siloxanes **5-8** are commonly described constituents of plant extracts.

Silicon-containing organic compounds such as silanes **1-3** and cyclic siloxanes **4-8** (Figure 1) have been reported as constituents of plant extracts from a large

number of plant species. Nevertheless, while silicon—in forms such as silica or silicic acid—is recognized as often a minor yet essential element for various organisms, including humans and plants [4] [5], playing a role in the regulation of the synthesis, metabolism, and modification of secondary metabolites [6], siloxanes and silanes found in biological samples are, for the most part, of anthropogenic origin. Their identification and their origin, as well as implications concerning their classification as xenobiotics are the subjects explored in this communication.



**Figure 2.** Linear permethylated siloxanes 9-13.

## 2. Methodology

In my time as reviewer of manuscripts on natural product isolation, time and again, I came across constituent compounds that appeared unlikely to be genuine natural metabolites. These include highly strained compounds such as cubanes, fluorinated cyclopropanes and boranes. Also, silane and siloxanes were frequently on the list of detected compounds. This led to a search utilizing the keywords “silane”, “silicone” and “siloxane” in combination with “natural product isolation” in the databases Scopus<sup>®</sup>, Web of Science<sup>®</sup> and SciFinder<sup>®</sup>. Subsequently, database searches were conducted using the most common substructures identified in the initial search—such as cyclosiloxanes of varying ring sizes, open-chain siloxanes, and silyl-substituted aromatics—employing a structural editor. The search results were further refined by incorporating the term “occurrence” and limiting the timeframe to the years 2009-2021. The pertinent manuscripts were acquired utilizing the resources



Linear siloxanes such as dodecamethylpentasiloxane (L5, **11**) are used in hair conditioners. Decamethyltetrasiloxane (L4, **10**) is used in cleaning agents and as an intermediate for other chemicals [17]. Tetradecamethylhexasiloxane (L6, **12**) is used as heat transfer agent. Low weight cyclosiloxanes are used as solvents and in personal care products. Octamethylcyclotetrasiloxane (D4, **5**) has historically been used on a large scale in personal care products including cosmetics, hair conditioners and emollients (moisturising creams) [18]. Global production was 136,000 tons in 1993 [19] and 340,200 - 453,600 tons in 2015 [20]. However, D4 (**5**) is now facing significant pressure from regulators. It is seen as a substance of very high concern in the EU, where it is classified as a PBT (persistent, bioaccumulative and toxic substance) and effectively banned in personal care products as of 2018. The US EPA began re-evaluating its risks in 2020 [21]. Decamethylcyclopentasiloxane (D5, **6**) is also considered an emollient. In Canada, of D5 (**6**) used in consumer products, approximately 70% were for antiperspirants and 20% for hair care products [22]. 10,000 - 100,000 tonnes per year of **6** is manufactured and/or imported in the European Economic Area [23]. Decamethylcyclopentasiloxane (D5, **6**) has also been tried as a dry-cleaning solvent in the early 2000s as a more environmentally friendly solvent replacement for tetrachloroethylene (the most common dry-cleaning solvent worldwide) despite being controlled in the EU due to its persistent, bioaccumulative and toxic characteristics [24]. Also, dodecamethylcyclohexasiloxane (D6, **7**) is used in cosmetics, specifically as a hair conditioning agent. As the ring size increases in compounds beyond D6 (**7**) the amount of the compounds produced and their practical applications decrease.

**Table 1.** Basic categories of siloxanes, their characteristic properties and typical applications.

Type of siloxane	Physicochemical character	Typical application/usage
Linear PDMS	Flexible, inert, hydrophobic	Medical implants [25], lubricants [26], soft robotics [27]
Cyclic siloxanes D4-D6	Volatile, low viscosity	Cosmetics, personal care products [28]
Branched/caged siloxanes	More rigid than PDMS, thermally stable	High-performance materials [29], coatings [30]

Many methylsiloxanes are quite volatile (**Table 2**) and can be released from personal care products (PCPs) into the air space directly. Concentrations of D4 (**5**) - D6 (**7**) have been measured in PCPs in Canada, USA, Japan and in China, with the highest concentrations found to be 11,000 µg/g for D4 (**5**), 683,000 µg/g for D5 (**6**), and 97700 µg/g for D6 (**7**) [31]. Also, methylsiloxanes are emitted as components of biogas from digesters [32] [33] at wastewater treatment plants [34] [35] and from solid waste landfills [32] [36] [37]. These siloxanes often stem from wastes of shampoos, soaps, surfactants, oils and pharmaceutical products which then are subject to anaerobic digestion processes. Overall, atmospheric emissions of D5 (**6**) in the Northern Hemisphere were estimated to be 30,000 tonnes per year [38]. Therefore, siloxanes are found in most environmental compartments. A composite of different studies [39] [40] give ranges of concentrations for D4 (**5**), D5 (**6**),

and D6 (7) in soils of industrial, residential and agricultural areas as 9-58.6 µg/g (D4, 5), 11 - 221 µg/g (D5, 6), and 7.5 - 1750 µg/g (D6, 7). In river water in Liaoning Province, North China, a combined concentration of  $14 \pm 6.3$  ng/L for siloxanes D4 (5), D5 (6), D6 (7), D7 (8), L4 (10), L5 (9) and L6 (11) [41] was measured. Measurements of siloxane concentrations in river water in Catalonia (Spain) gave values of 0.09 to 3.94 ng/L for linear siloxanes and 22.2 to 58.5 ng/L for cyclic siloxanes [42]. A total concentration of 2200 ng/m<sup>3</sup> for D4 (5), D5 (6), and D6 (7) was measured in the indoor air space of the Seaman's Center of the University of Iowa, Iowa City, USA. Outdoor measurements of siloxanes come from Chicago, Cedar Rapids (Iowa, USA), and West Branch (Iowa, USA), showing median sum siloxane levels of 280, 73, and 29 ng/m<sup>3</sup>, respectively [43]. In the atmosphere, the long range transport of cyclosiloxanes has been investigated [44]. Altogether, this means that siloxanes are ubiquitous contaminants that are present in our environment in appreciable quantities.

Nevertheless, it must be noted that siloxanes degrade in the natural environment, mostly through hydrolysis and final oxidation of silicon to finally give silica. Reported half-lives in water are 16.7 days (d) for D4 (5, water solubility around 51 µg/L) at pH 7 and 12°C in freshwater, and 2.9 d at pH 8 and 9°C in marine water, 73.4 d for D5 (6, water solubility 17 µg/l at 23°C), > 1 year for D6 (7, water solubility 5.13 µg/l at 25°C), the latter two in freshwater at pH7 and 25°C. Half lives in the atmosphere are given as 6.9 - 16.9 d for D4 (5), 6.2 - 11.0 d for D5 (6), 5.7 - 8.9 d for D6 (7), and 8.7 - 30.9 d for hexamethylcyclotrisiloxane (D3, 4) [45]-[48].

There has been targeted research of the occurrence of siloxanes in biota such as in the Crucian carp (*Carassius auratus*) around a siloxane producing plant [41], in archived German fish samples covering a period of two decades [49], and in the planktonic crustacean *Daphnia magna* [50]. In the case of the crucian carp, 7 carp specimen each were collected from 7 sites along a river near a methylsiloxane producing plant in Liaoning Province, Northeast China. Concentrations of 6.5 - 18 ng/g D4 (5), 12 - 25 ng/g D5 (6), 5.0 - 13 ng/g D6 (7), 1.5 - 41 ng/g D7 (8), 0.58 - 2.0 ng/g L4 (10), 0.66 - 0.93 ng/g L5 (9), 0.45 - 1.0 ng/g L6 (11) were measured in the back muscle tissue of the fish [41]. Only for D4 (5) an appreciable bioaccumulation potential was observed in the fish. Archived German fish samples partially showed higher siloxane contents with samples from a Saar river sampling at Gündingen (downstream the French-German border) of 1997 exhibiting 91 ng/g (ww) D4 (5), 6640 ng/g (ww) D5 (6) and 63 ng/g ww D6 (7) [49]. In the third study, D4-D6 had been found in palm oil mill effluent, with D4 being detected at 0.0148 - 0.0357 mg/L, and the crustacean *Daphnia magna* was used for toxicity identification evaluation (TIE) tests upon being exposed to the effluent [50]. In all 3 studies [41] [49] [50], it was made clear that the siloxanes detected were of anthropogenic origin.

While especially the high molecular weight silicones (siloxanes), often also used in medical applications are deemed little toxic to humans [51], at high doses, it has been found that volatile methylated silicones can affect animals' reproductive

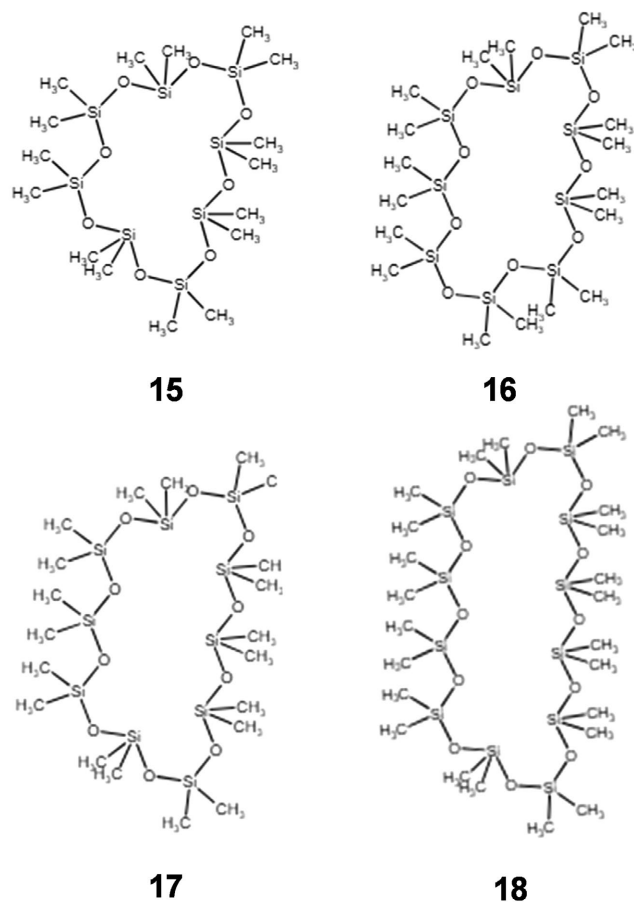
and endocrine systems [52] [53], are carcinogenic, where especially D5 was shown to increase the incidence of the uterine adenocarcinoma in female rats [54], and harm the respiratory tract [13] [55]. Indeed, safety concerns increase with a decrease in size of the siloxanes, so that the greatest concern rests with smaller sized molecules such as the linear and cyclic siloxanes shown in **Figure 1** and **Figure 2** as low molecular weight silicones are more volatile, can change the structure of lipid bilayers by fluidization or even the extraction of lipids [56] [57] leading to irreversible damage of the stratum corneum [58] and can weaken cell membranes [56]. In general, the vapor pressures of the linear siloxanes and the cyclic siloxanes are appreciable (**Table 2**). Low molecular weight silicones can accumulate in the organism, and can have a long-term effect on organs [59]. Volatile siloxanes can reach the lungs and hydrolyze. It must be noted that silica itself is not without its toxicity—direct inhalation of silica can lead to silicosis—where the degree of chemical interaction between silica particles and biomolecules, membranes, and cell systems may be determined by their surface, namely by the positioning of silanol (Si-OH) functions on the surface [60].

**Table 2.** Boiling points and vapor pressures of the most common linear and cyclic polymethylsiloxanes. [a]: ECHA data; [b]: data from Lei *et al.*, 2010 [61].

Name	Boiling point	Vapor pressure
Hexamethylcyclotrisiloxane (D3, <b>4</b> )	134 °C	671 Pa (25 °C) [a]
Octamethylcyclotetrasiloxane (D4, <b>5</b> )	175 °C - 176 °C	124.5 ± 6.2 Pa (25 °C) [b]
Decamethylcyclopentasiloxane (D5, <b>6</b> )	210 °C	20.4 ± 1.1 Pa (25 °C) [b]
Decamethyltetrasiloxane (L4, <b>9</b> )	194 °C	73 Pa (25 °C) [a]
Dodecamethylpentasiloxane (L5, <b>11</b> )	230 °C	7.8 Pa (25 °C, pred.) [a]
Tetradecamethylhexasiloxane (L6, <b>12</b> )	246.1 °C	0.74 Pa (30 °C) [a]

In comparison to siloxanes (silicones), silanes are much less common constituents in final products as silanes are inherently less stable than siloxanes. More often, compounds such as 1,2-bis(trimethylsilyl)benzene (**2**) are used as chemical starting materials. Thus, 1,2-bis(trimethylsilyl)benzene (**2**) itself is used as a precursor to benzyne and in the construction of luminescent  $\pi$ -conjugated materials [62]. 1,4-Bis(trimethylsilyl)benzene (**3**) has been forwarded as an additive in batteries with high performance solid-state electrolytes [63] and in semi-conducting devices [64]. It also has been used as a precursor for developing silicon carbide coating using plasma-assisted chemical vapor deposition (CVD) process [65]. There are fewer studies on hazards aryl- and alkylsilanes pose. It must be noted that aryl- and alkylsilanes for the most part are highly flammable [66]. They are also strong irritants to skin [67], eyes [67] [68] and the respiratory system [67]. Many of the aryl- and alkylsilanes can have long lasting harmful effects to aquatic life [69].

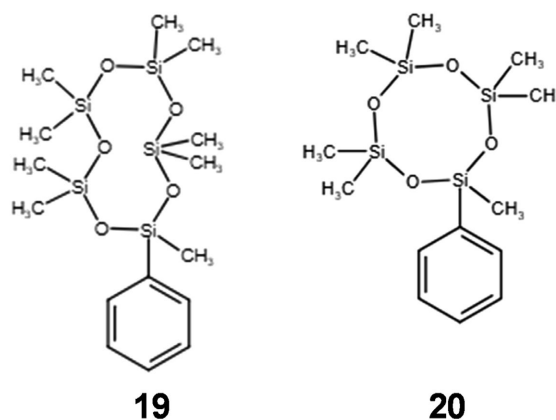
### 3.2. Siloxanes and Arylsilanes Isolated from the Essential Oil of Plants and from Other Organisms



**Figure 4.** Structures of larger cyclosiloxanes D8 (15) - D12 (18).

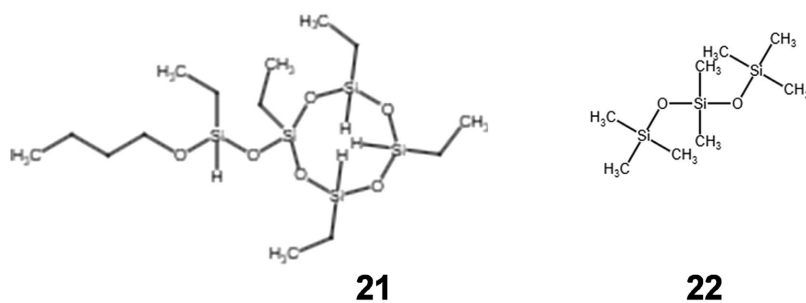
There have been reports of silylated compounds isolated from plants and other organisms (Table 3-5), where the authors have not commented on whether these compounds constitute actual phytochemicals/metabolites of natural origin, anthropogenic contaminants deposited on the plant material before collection or contamination stemming from the GC/MS analysis itself. Beneficial properties, e.g. antimicrobial properties, were ascribed to some of the silylated components within isolated essential plant oils as would typically be done for selected secondary plant metabolites exhibiting those traits, with the unspoken perspective that the silylated compounds necessarily belong to the metabolites produced by the plant or microorganism itself. These silylated compounds can be broken down into three main categories: a) small per-methylated cyclosiloxanes; b) open chain per-methylated siloxanes; and c) silylated aromatic compounds. In addition, there is a set of miscellaneous silylated compounds such as silylated cycloheptatrienones. There are examples of silylated compounds that have been reported to have been isolated that are rather instable such as structures that exhibit Si-H moieties, where the identity of the compounds may be in doubt.

By far the most found silyl-substituted compounds in plants, fungi, bacteria and other organisms are the cyclic permethylated siloxanes D3 (**4**) [70]-[86], D4 (**5**) [71] [76] [78] [87]-[90], D5 (**6**) [70] [71] [87]-[89] [91]-[98], and D6 (**7**) [76] [87]-[89] [91] [94]-[96] [98]-[108] (**Table 3**), which are at the same time the most released silyl-containing contaminants from anthropogenic activities (see above). Also, permethylated cyclosiloxanes D7 (**8**) [78] [88] [89] [91] [96]-[99] [102]-[104] [106] [109], D8 (**15**) [71] [95]-[97] [101] [102] [109]-[111], D9 (**16**) [91] [95]-[97] [100] [104] [107] [109], D10 (**17**) [95] [96] [100] and D12 (**18**) [91] have been isolated (**Table 3**, **Figure 2** and **Figure 4**).



**Figure 5.** Monophenylated cyclic siloxanes **19** and **20**.

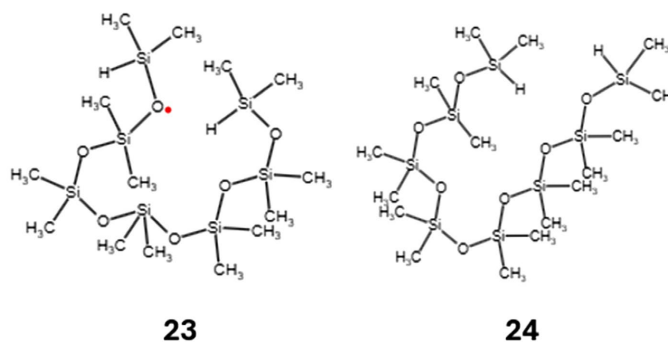
Other non-permethylated cyclic siloxanes have been isolated from organisms such as the two mono-phenylated cyclosiloxanes nonamethylphenylcyclopentasiloxane (**19**) and heptamethylphenylcyclotetrasiloxane (**20**) from the leaves of the green amaranth (*Amaranthus viridis* Linn.) [104] (**Figure 5**). The leaf extracts held a number of other siloxanes such as D6 (**7**) and D7 (**8**) [104]. Other structures have not been unequivocally defined and/or exhibit Si-H bonds. Such an example is 1.3.5.7-tetraethyl-1-ethylbutoxysiloxycyclotetrasiloxane (**21**) [91] (**Figure 6**).



**Figure 6.** Structure of 1.3.5.7-tetraethyl-1-ethylbutoxysiloxycyclotetrasiloxane (**21**), isolated from Egyptian cauliflower (*Brassica oleracea* var. Botrytis) [91] and of octamethyltrisiloxane (**22**) isolated from Siberian fritillary (*Fritillaria pallidiflora*) [112].

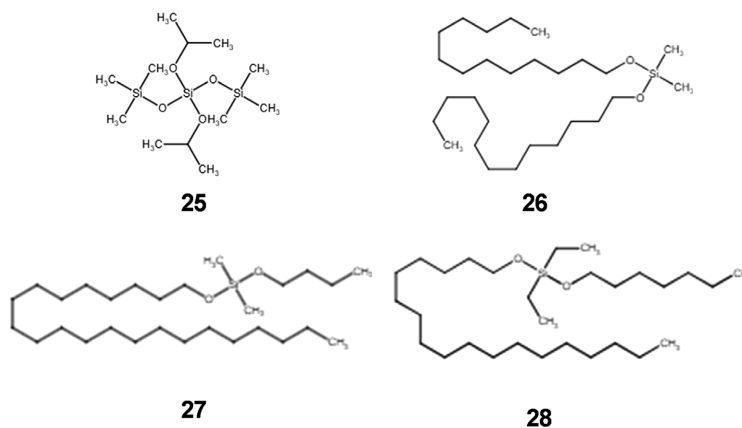
The isolation of linear permethylated siloxanes from plants and other organisms have been reported less frequently than that of permethylated cyclosiloxanes.

Nevertheless, isolation of octamethyl-trisiloxane (**22**) [112], decamethyltetrasiloxane (**10**) [78] [85] [86] [112], dodecamethyl-pentasiloxane (**9**) [91], tetradecamethyl-hexasiloxane (**11**) [91], hexadecamethyl-heptasiloxane (**12**) [81], and octadecamethyl-octasiloxane (**13**) [113] is known. A number of papers have appeared where the names of non-permethylated linear siloxanes have been forwarded leading to structures such as compounds **23** [80] and **24** [80] [96] [101] shown in **Figure 7**, all with a Si-H group at both termini. Some of these, however, may have been mistakenly labelled and may have meant to be permethylated cyclosiloxanes.



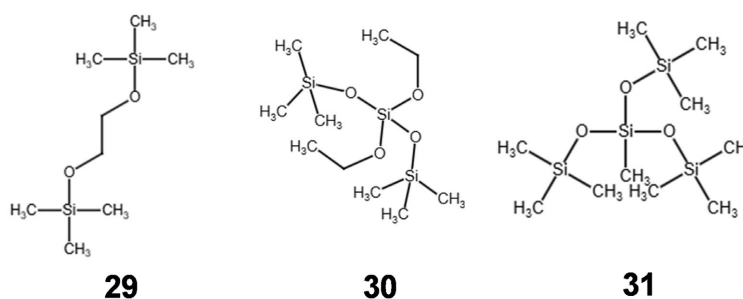
**Figure 7.** Non-permethylated linear siloxanes **23** and **24**.

3,3-Diisopropoxy-1,1,1-5,5,5-hexamethyltrisiloxane (**25**) is a hydrophobic substance that is used as an ingredient for coatings to make water-repellent and oil-repellent surfaces. It has been found in false water willow (*Pteridium aquilinum* L.) [82], eagle fern (*Andrographis echioides*) [114], and the evergreen tree Akpi (*Blighia unijugata*) [86]. Silanes with two small alkyl chains and two extended alkoxy groups such as **26-28** are also typically used as surface treatment agents, especially in coatings, plastics, or composite materials. Thus, dimethyl[bis(tridecyloxy)]silane (**26**) is utilized on glass, metal, or ceramic surfaces to impart water- and oil-repellent properties (**Figure 8**). **26-28** have been isolated from the flowering plant Solomon's seal (*Polygonatum cirrhifolium* (Wall.) Royle) [97].



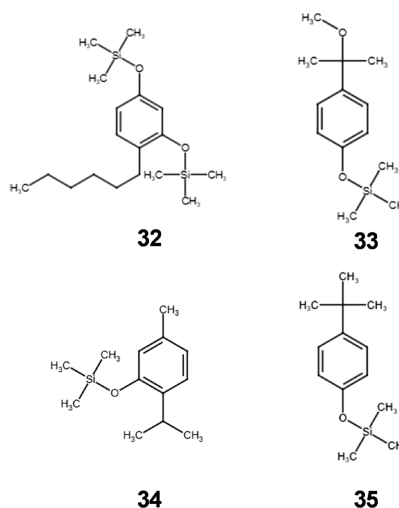
**Figure 8.** Structures of 3,3-diisopropoxy-1,1,1-5,5,5-hexamethyltrisiloxane (**25**) and dialkoxysubstituted silanes **26-28**.

Small-sized siloxanes such as the volatile 1,2-bis(trimethylsiloxy)ethane (**29**) and small sized silicates such as diethyl bis(trimethylsilyl) silicate (**30**) are found less in consumer goods. Diethyl bis(trimethylsilyl) silicate (**30**) is used as a silylating agent and as a cross-linking agent in the silicone industry in controlled reaction spaces. There are but few occasions where either of the compounds have been isolated from plants, however (**Table 3**). **29** has been isolated from the common barberry (*Berberis vulgaris*) [115], **30** from the essential oil of the flowers of *Blighia unijugata*. On the other hand, methyltris(trimethylsiloxy)silane (**31**, MTTMS and also known by trade names like Dynasylan<sup>®</sup>) is often used to make surfaces water-repellant and is also frequently used in photoresist formulations and for low-k dielectric materials. **31** has been isolated from the essential oil of the bark of *Blighia unijugata* and from fermented honeyberry (*Lonicera edulis*) [116] (**Figure 9**).



**Figure 9.** Structures of compounds 29-31.

A large variety of *O*-silylated phenols (trialkylsiloxybenzenes) have been communicated as plant constituents, especially *O*-trimethylsilylphenols. Some of these are shown in **Figure 10**. **32** has been isolated from the oil of the seed oil of the tea oil camellia (*Camellia oleifera*) [90], **33** has been obtained from knicker nut (*Caesalpinia bonducella*) [79], **34** from *Blighia unijugata* [86], and **35** from Karchikai (*Momordica cymbalaria*) [74].



**Figure 10.** Structures of *O*-TMS substituted phenols 32-35.

A number of *tert*-butyldimethylsilyl (TMDMS-) substituted compounds have been isolated from plants (Figure 11), including *O*-*tert*-butyldimethylsilyl substituted alcohols and acids and *N*-*tert*-butyldimethylsilyl substituted amines. Typical examples are 2-chloro-6-fluorobenzyl alcohol *tert*-butyl dimethyl silyl ether (38) from the fern *Pteridium aquilinum* (L.) [114], benzenepropanoic acid *tert*-butyldimethylsilyl ester (37) from Karchikai (*Momordica cymbalaria*) [74], 2-[(*tert*-butyldimethylsilyl)oxy]-1-isopropyl-4-methyl-benzene (39) from the essential of the stem bark of *Blighia unijugata*, a flowering plant in the soapberry family [86], as well as *N*-(*tert*-butyldimethylsilyl)-1,2-benzisothiazol-3-amine (36) from the seeds of the knicker nut *Caesalpinia bonducella* [79] and volatiles of fermented elephant foot yam roots and tubers [98], and 3-chloropropane-1,2-diol bis(*tert*-butyldimethylsilyl) ether (40) from the roasted seed oil of *Camellia oleifera* [90], 36 and 40 having been isolated from processed plant material [90,98]. It must be noted that 1,2-benzisothiazol-3-amine itself is utilized in the synthesis of agrochemicals [117]. *Tert*-butyldimethylsilyloxy compounds are typically seen as hydroxy-protected molecules, in which the *tert*-butyldimethylsilyl (TBDMS) group serves as a protective group of an alcoholic or phenolic OH group [118]. It is less often used for the protection of a carboxylic acid function [119]. Compared to the trimethylsilyl (TMS) group, the TBDMS group is less susceptible to hydrolytic deprotection. Silyloxy groups in general can be deprotected facilely with fluoride anion, e.g., with the reagent tetrabutylammonium fluoride (Bu<sub>4</sub>NF). Nevertheless, as *tert*-butylsilylating agents such as *tert*-butyldimethylsilyl chloride are relatively expensive, *O*-*tert*-butylsilyl functions as protective groups are usually only found in small scale syntheses and siloxanes with *tert*-butyldimethylsilyloxy groups in commercial products are rare indeed.

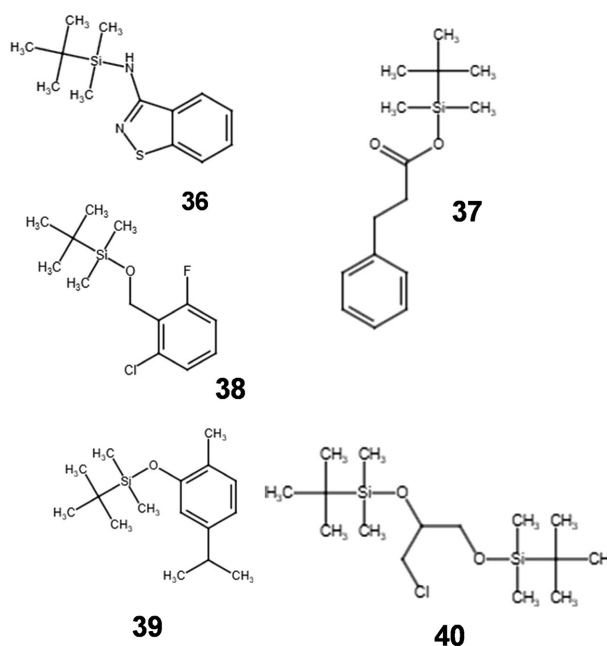
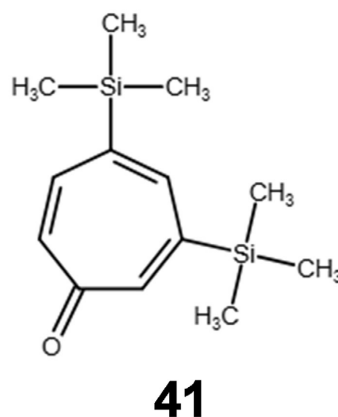


Figure 11. Examples of *O*-*tert*-butyldimethylsilyl amine (36), ester (37) and ethers (38-40).

Directly C-silylated aromatic compounds have also been isolated from plants frequently. These include especially 1,2-bis(trimethylsilyl)benzene (**2**) [72]-[75] [77]-[81] [84]-[86] [122]-[128], 1,3-bis(trimethylsilyl)benzene (**1**) [83] [86] [121], and 1,4-bis(trimethylsilyl)benzene (**3**) [72] [74] [79] [85] [112] [124] (**Figure 1**) Where bis(trimethylsilyl)benzenes **1-3** have been extracted from a natural source, oftentimes other siloxanes were found, too. Typical examples are the extraction of **2** from the medical plant *Abrus precatorius* (jequirity bean/rosary pea, Faboideae), where hexamethylcyclohexatrisiloxane (**4**) was also found [83]. 1,4-Bis(trimethylsilyl)benzene (**3**) is utilized industrially as a silicon-containing precursor in chemical vapor deposition (CVD) processes to make thin films of silicon-based materials like silicon oxide, nitride, or carbide. 1,2-Bis(trimethylsilyl)benzene (**2**) is a key starting material for the synthesis of efficient benzyne precursors and certain luminescent  $\pi$ -conjugated materials [60]. However, both compounds are not produced in large amounts industrially, and for the most part, however, they are not constituents of consumer products.

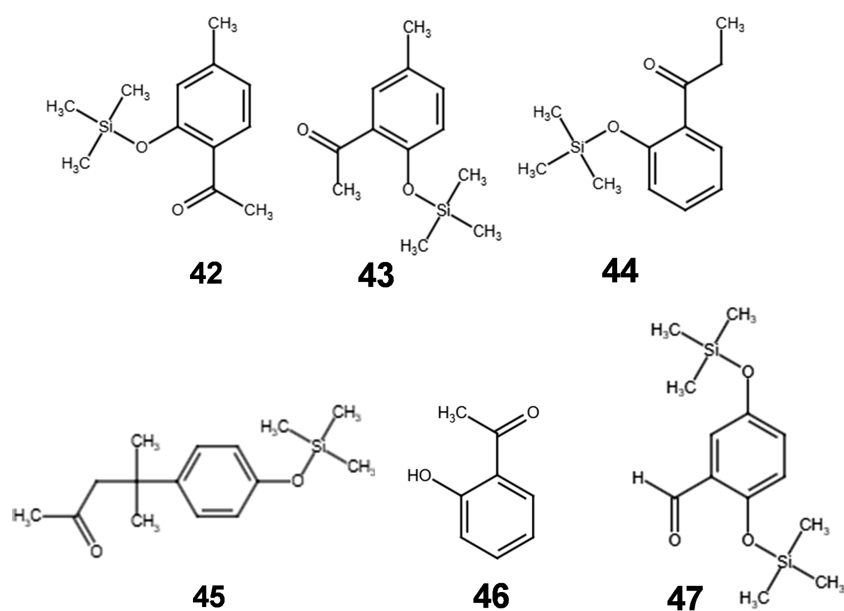


**Figure 12.** Structure of 3,5-bis(trimethylsilyl)cycloheptatrienone [3,5-bis(trimethylsilyl)troponone] (**41**).

Interestingly, 3,5-bis(trimethylsilyl)cycloheptatrienone [3,5-bis(trimethylsilyl)troponone] (**41**) (**Figure 12**) is another product that purportedly has been found in a number of plants, such as in *Amomum nilgircum* (Zingiberaceae) [129], *Dillenia scabrella* (Dilleniaceae) [78], *Boerhavia diffusa* (Nyctaginaceae) [130], and the common guava (*Psidium guajava*) [131]. Now, there are no obvious large-scale applications or large scale industrial outputs of 3,5-bis(trimethylsilyl)cycloheptatrienone (**41**). In many scientific contributions on the isolation of **41**, only the GC trace is shown, where the compound has been identified through a database by its molecular mass and retention time on the GC column used. Only in one case is the fragmentation pattern of the compound shown. There are instances where the quality of match of the obtained analytical data of the compound against existing mass spectral databases is relatively low (see below).

Silylated arylketones such as 4-methyl-2'-trimethylsilyloxyacetophenone (**42**) [80] [85], 5-methyl-2'-trimethylsilyloxyacetophenone (**43**) [80] [85] [98] [121], 2'-

trimethylsilyloxypropiophenone (**44**) [74] [79] [86], and trimethyl[4-(2-methyl-4-oxo-2-pentyl)phenoxy]silane (**45**) [79] [86] [132] (**Figure 13**) are frequently isolated from plants and processed plant-based food [132]. Here, it must be noted that Penduka *et al.* [85] has treated hexane extracts of bitter kola (*Gardicinia kola*) seeds with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) (pyridine/dichloromethane) in order to make the constituents more volatile and amenable to GC-MS spectrometric analysis (see below), which would convert hydroxyarylketones to siloxyarylketones. One of the starting materials for this conversion, 2'-hydroxyacetophenone (**46**), is a constituent of essential oils of plants and can be found in *Carissa spinarum* [133] and of *Carissa lanceolata* R.Br. [134]. It has also been detected in different foods, such as in green tea, arabica coffees (*Coffea arabica*), Chinese cinnamons (*Cinnamomum aromaticum*), cocoa beans (*Theobroma cacao*), and cocoa and cocoa products. It is a typical flavor additive for cherry kernel, rum, tobacco, and tropical fruit. A further silylated carbonyl substituted aromatic compound found in plants is 2,5-bis(trimethylsilyl)benzaldehyde (**47**), which was found in the volatiles of sweet corn (*Zea mays*) juice [120].

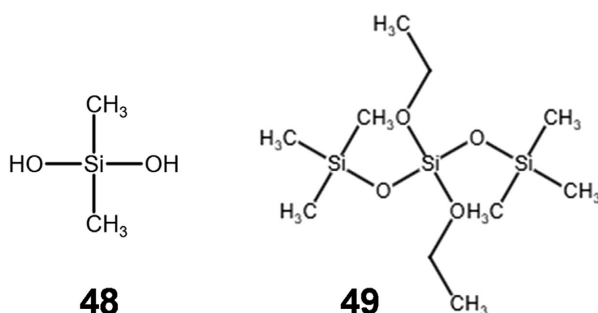


**Figure 13.** Structures of silylated hydroxyarylketones **42-45**, 2' hydroxyacetophenone (**46**) and 2,5-bis(trimethylsilyl)benzaldehyde (**47**).

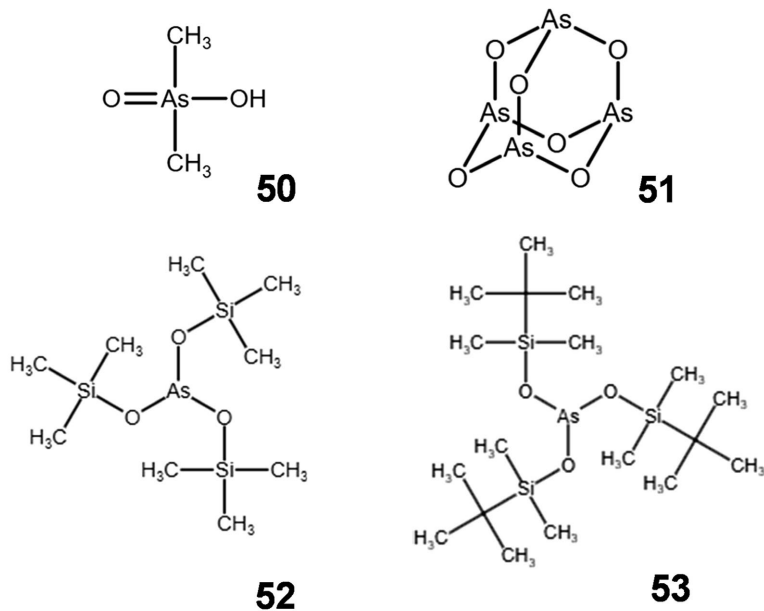
Dimethylsilanediol (**48**, **Figure 14**) was found in the volatiles from cultured purple sweet corn (*Zea mays*) [120]. Dimethylsilanediol is an industrial intermediate produced in large quantities (high production volume compound [HPVC]) for the synthesis of silicones. It is not available commercially and therefore is not considered a consumer product or an ingredient in consumer products. Due to its chemical structure, it readily undergoes condensation to form polysiloxanes (silicones). On the other hand, interestingly, compounds such as hexamethyldisiloxane [135], octamethylcyclotetrasiloxane [136], and decamethylcyclopentasiloxane [135] are

known to metabolize into dimethylsilanediol through pathways that may also occur in the human body.

A further compound that is produced and used industrially in large amounts is silicic acid diethyl bis(trimethylsilyl) ester (**49**), where uses include surface treatments, coatings, and as a precursor in the production of other organosilicon compounds. **49** has been found in Karchikai vine (*Momordica cymbalaria* Hook. F.) [74] and in knicker nut (*Caesalpinia bonducella*) [79].



**Figure 14.** Structure of dimethylsilane-diol (**48**) and of silicic acid diethyl bis(trimethylsilyl) ester (**49**).



**Figure 15.** Structures of dimethylarsinic acid (**50**), arsenic trioxide (**51**), arsenous acid tris(trimethylsilyl) ester (**52**), and arsenous tris(*tert*-butyl dimethylsilyl) ester (**53**).

Looking at silylated inorganic compounds isolated from plants, derivatives of arsenous acid and arsenic trioxide stand out (**Figure 15**). While dimethylarsinic acid (cacodylic acid, **50**) and its sodium salt are known herbicide, the anhydride form of arsenous acid, arsenic trioxide (**51**), is used as a herbicide, pesticide, and rodenticide [134]. Arsenous acid tris(trimethylsilyl)ester (**52**) and its tris(*tert*-butyl dimethylsilyl) derivative **53** are usually only utilized as silylating reagent in organic syn-

thesis. Although the oxygen of siloxanes can coordinate with electrophiles  $E^+$ , it would be unlikely that arsenic trioxide would react with siloxanes or with degradation products of the Zebron-5MS column (5%-phenylmethylpolysiloxane) that was used in the separation of the extracts, especially as there is no source of the *tert*-butyldimethylsilyl group in evidence. Therefore, **52** and **53** isolated from black jack (*Bidens pilosa*) [80], from fermented elephant foot yam roots and tubers (*Amorphophallus paeoniifolius*) [132] and from Karchikai-vine (*Momordica cymbalaria* Hook. F.) [74] may be of different origin.

Additional silylated compounds that have been isolated from plants, but are not discussed further in the text can be seen in **Figures 19-21**.

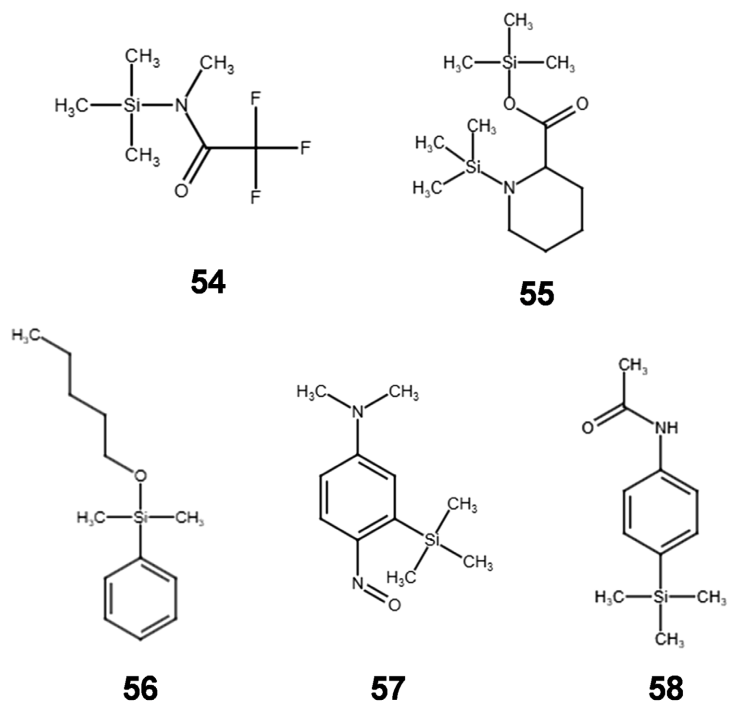
### 3.3. Potential Sources of Siloxanes and Arylsilanes Isolated from the Essential Oil of Plants and from Other Organisms

The origin of siloxanes and arylsilanes in extracts from natural sources can be manifold. It is notable that oftentimes more than one type of silicon containing compound was isolated in different studies. Thus, Mostafa *et al.* [113] found 3 different siloxanes in the methanolic leaf extract of the olive (*Olea europea*), octamethylcyclotetrasiloxane (D4, **5**), decamethylcyclopentasiloxane (D5, **6**), and octadecamethyl-octasiloxane (octasiloxane, L8, **13**), which made up 14.7% of the identifiable components of the extract. Thenmozhi *et al.* [79] isolated 10 different silyl-containing compounds from the seed kernels of the knicker nut (*Caesalpinia bonducella*). The following is a discussion of possible sources of silyl-containing compounds from natural sources.

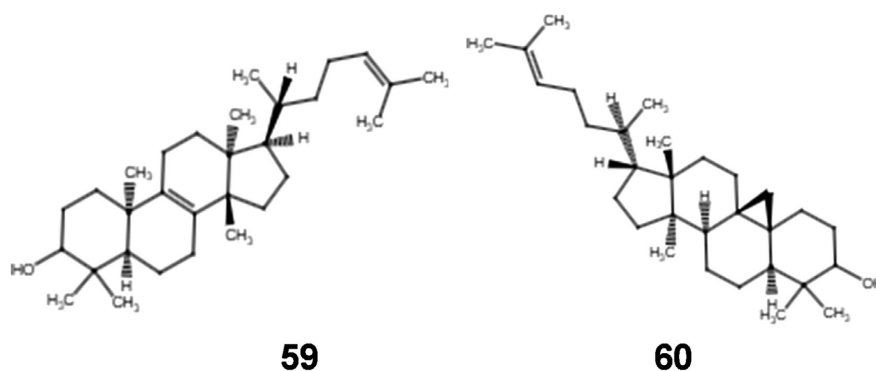
a) Targeted silylation of samples before injection of the samples for GC-MS chromatographic analysis

Sometimes, the GC separation of very polar compounds during GC-MS spectroscopic analysis requires TMS derivatization [138] [139]. Thus, Penduka *et al.* [85] have silylated the samples before GC/MS analysis utilizing *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (**54**, MSTFA) (pyridine/dichloromethane) (**Figure 16**). This explains the formation of such products as 1-trimethylsilyl-2-piperidinecarboxylic acid trimethylsilyl ester (**55**), 4-methyl-2-trimethylsilyloxyacetophenone (**42**), and 5-methyl-2-trimethylsilyloxyacetophenone (**43**), where these products may well not have been silylated in the original extract as well as trimethyl[4-(1-methyl-1-methoxyethyl)phenoxy]silane (**33**), trimethyl-(4-*tert*-butylphenoxy)silane (**35**), silicic acid diethyl bis(trimethylsilyl) ester (**49**), and perhaps of methyltris(trimethylsilyloxy)silane (**31**). This is also indicated by the authors. In addition, there is 1-dimethyl(phenyl)silyloxy-pentane (**56**) which does not stem from MSTFA treatment. Directly silylated arenes such as *N,N*-dimethyl-4-nitroso-3-(trimethylsilyl)aniline (**57**), *N*-[4-(trimethylsilyl)phenyl]acetamide (**57**) and 1,2-bis(trimethylsilyl)benzene (**2**) do not stem from MSTFA treatment, either. Direct C-silylation of arenes is still very rare, and 1,2-bis(dimethylsilyl)benzene (**2**) is still best synthesized from 1,2-dibromobenzene using Rieke-magnesium [60]. Interestingly, Penduka *et al.* [85] identified the triterpenols lanosterol (**59**) and 9,19-cyclolanost-24-en-3 $\beta$ -ol

(60) (Figure 17) in the extracts after treatment with MSTFA as the alcohols themselves and not as their silyl ethers. In none of the other cited studies did the authors note that a silylation of the mixed plant extract had been carried out prior to GC/MS analysis.



**Figure 16.** Silylated compounds 54 – 58, identified by GC-MS after treating the n-hexane extracts from the seeds of bitter kola (*Gardicinia kola*) with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) [85].

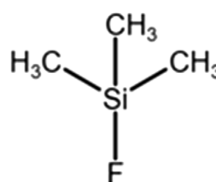


**Figure 17.** Structures of the triterpenols lanosterol (59) and 9,19-cyclolanost-24-en-3β-ol (60), which were analyzed non-silylated after treatment of n-hexane extracts from the seed of bitter kola (*Gardicinia kola*) with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) [85].

#### b) Siloxanes derived from the GC-MS spectroscopic analysis

There are 4 basic sources of siloxanes entering the system in the gas chromatographic separation: the column itself, injector liners, septa and vial caps. In the case

of a 100% dimethylpolysiloxane SE-30 column, bleeding does generate siloxanes that convert partially to D3 and in EI-mode give  $m/z$  207 as the top peak [140], so that the presence of a peak with  $m/z$  207 can be indicative of column bleeding [141]. Other ion peaks can be found at  $m/z$  73, 133, 193, 267, 281, 355 and 429, where D4 has its top peak at  $m/z$  281 [142], D5 at  $m/z$  355 [143], and D6 at  $m/z$  429 [144]. Analytes can also damage columns. Thus, fluorotrimethylsilane (**61**) (Figure 18) which is used as a fluorinating agent has been isolated from the volatiles of fermented honeyberry (*Lonicera edulis*). It is easily hydrolyzed, so that it would be likely that the compound is produced in the column in the presence of fluoride anion. The reaction would be equivalent to a fluoride induced desilylation of a trimethylsilyl ether, which can be achieved by tetrabutylammonium fluoride (TBAF). Fluoride containing samples could also potentially damage SE-30 columns for gas chromatography. Also, septa very often incorporate silicones which can be released upon interaction with organic solvents [145]. This happens especially during re-use of septa and vial caps. Also, valves and solvents can be sources of silicones and silanes.

**61**

**Figure 18.** Structure of fluorotrimethylsilane (trimethylsilyl fluoride, **61**).

c) Anthropogenic sources of silyl-containing compounds on plants and other organisms

The human driven emission of siloxanes into the environment has been mentioned in the introduction and is subject of a larger number of publications [8] [9] [13] [146]. The presence of typically used siloxanes in plants such as permethylated cyclosiloxanes D3-D8 and linear permethylated siloxanes L3-L8 may often be attributed to anthropogenic pollution. Even under ideal conditions, identifying the source of a specific contaminant or determining whether a compound is a true plant-derived metabolite or merely a contaminant is extremely challenging. Therefore, when uncertainty exists, authors should explicitly acknowledge it rather than present a silicon-containing compound as a natural metabolite. This is especially true when plant components are screened for their biological properties to understand the medicinal value of the plant itself. Thus, 4-methyl-2-trimethylsilyloxyacetophenone (**42**) and *tert*-butyl-(5-isopropyl-2-methylphenoxy)dimethylsilane (**39**) have been published to have antimicrobial properties [79] [80]. Overall, it must also be noted that the ubiquity of siloxanes in the environment may have adverse effects on human health [147].

d) misidentification through insufficient matching of mass data with mass spectral databases

One needs to take care when identifying organic compounds from mixtures solely by GC-MS. Where retention indices are often used to corroborate spectral matches, variations in experimental conditions can cause discrepancies between experimental and database RIs, leading to false positives. A study highlighted that even with a match score of 98%, there remains a significant probability of misidentification, particularly when the match score is below 80%. As an example, the quality of the match for 1,2-bis(trimethylsilyl)benzene (**2**) as a volatile constituent in the methanolic extract of *Rumex nervosus* meal was reported as 50% [84]. Employing algorithms that consider the difference between the first and second highest spectral similarity scores can reduce false positives. This approach has been shown to achieve higher true positive rates compared to conventional methods. Using multiple, curated databases and incorporating MS/MS data can enhance the reliability of compound identification [148]. Tools like MS-FINDER facilitate this by integrating various databases and in silico fragmentation data [149].

e) actual organic silane and siloxane plant metabolites—are they possible?

Silicon (Si) is recognized as a beneficial element for plants, known to mitigate both abiotic stresses—such as drought and high soil salinity—and biotic stresses, including fungal infections. Making up 28% of the composition of the earth's crust, silicon is the second most abundant element, existing mostly in form of silica ( $\text{SiO}_2 \cdot n \text{H}_2\text{O}$ ), silicates  $[\text{SiO}_{4-x}^{(4-2x)-}]_m$ , including aluminosilicates  $(\text{MAlO}_2)(\text{SiO}_2)_x(\text{H}_2\text{O})_y$  and silicic acid  $([\text{SiO}_x(\text{OH})_{4-2x}]_n)$ . Plants have been noted to absorb silicon exclusively in the form of monomeric silicic acid (ortho-silicic acid),  $\text{Si}(\text{OH})_4$ , at  $\text{pH} < 9$  [6] [150], where the silicon content in plants varies widely among species, ranging from 0.1% to 10% of dry weight [6] [151] [152]. The ability of plants to absorb Si is linked to the presence of specific transporter proteins [150]. Si transporters are elusive in all forms of life, and have been identified only in diatoms [153] and more recently in the roots of some higher plants, including rice (*Oryza sativa* L.), barley (*Hordeum vulgare* L.), wheat (*Triticum aestivum* L.) and pumpkin (*Cucurbita moschata* Duch.) as well as the common horsetail (*Equisetum arvense*) [146] [154]-[156]. Si is then carried by the plants' vascular system to the cell walls, cell lumen, and intercellular spaces. It is known that silicic acid can oligomerize easily, where processes are known whereby deposited silicic acid condenses to silica [157], growing phytoliths, silica deposits in certain plant tissues, within and between the epidermal cells [158] [159]. Silicon helps regulate the production of secondary plant metabolites to give the plant enhanced tolerance to biotic and abiotic stresses. It has been shown that Si upregulates enzymes such as phenylalanine ammonia lyase (PAL), chalcona synthase (CHS), polyphenoloxidase (PPO), peroxidase (POD) [160]-[165]. The exact molecular mechanism of Si with these enzymes is still poorly understood [166]. This is in contrast to the understanding of the role of other non-CHNO elements such as the metalloid selenium (Se) where for instance it is known that selenocysteines incorporated in proteins often serve as catalytic centers for biochemically crucial redox processes [167].

It is important to note, however, that no silicon-containing natural secondary plant metabolite has been unequivocally identified—meaning that no novel silicon-containing structure that has not yet been synthesized industrially or in a research laboratory setting has been isolated from a plant or other organism and structurally characterized using NMR, IR, and MS spectroscopy, nor have feeding experiments with labeled precursors been conducted that clearly demonstrate the incorporation of silicon into organic structures in a defined manner by the organism. Thus, while sulfur containing amino acids such as cysteine, cysteine and methionine as well as selenoamino acids such as selenocysteine [168] are known and arsinothricin as a non-proteinogenic arsenoamino acid has been isolated from the rice rhizosphere bacterium *Burkholderia gladioli* strain GSRB05 fed with medium containing arsenite (As<sup>III</sup>) [169] [170], no such silicon containing amino acid has been found to date. Si much prefers to bond with oxygen (O) than with carbon (C). A Si-C bond (~318 kJ/mol) is weaker than a comparable C-C bond (~348 kJ/mol (stronger)), while a Si-O bond (~452 kJ/mol) is significantly stronger than a comparable C-O bond (~358 kJ/mol), making the Si-O bond extremely stable, while Si-C bonds are more reactive than C-C bonds, particularly to hydrolysis, reactions that ultimately lead to silica, making silicon containing metabolites, should they to exist, very elusive species.

**Table 3.** List of organic silanes and siloxanes isolated from plants, fungi, bacteria and other organisms.

Name of isolated compound	Latin name of the organism	Common name of the organism	Fraction in which the compound was isolated from	Type of analysis	Location	Reference
Hexamethylcyclotrisiloxane (D3,4)	<i>Juglans regia</i>	Walnut	green husks	GC/MS	West Anatolia, Turkey	D. Keskin <i>et al.</i> , 2012 [70]
Hexamethylcyclotrisiloxane (D3,4)	<i>Phyllostachys heterocyclus</i> ( <i>Phyllostachys edulis</i> )	Bamboo	biomass	GC/MS	China	Q.Z. Ma <i>et al.</i> , 2010 [71]
Hexamethylcyclotrisiloxane (D3,4)	<i>Vernonia amygdalina</i>	Bitter leaf	leaf extract	GC/MS	Elizade University, Ilara-mokin, Ondo state, Nigeria	O.S. Omojokun <i>et al.</i> , 2019 [72]
Hexamethylcyclotrisiloxane (D3,4)	<i>Sesamum indicum</i> L	Sesame (Pedaliaceae)	Seeds (light petroleum ether extract)	GC/MS	different states of India	R. Tyagi and V. Sharma, 2014 [73]
Hexamethylcyclotrisiloxane (D3,4)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]
Hexamethylcyclotrisiloxane (D3,4)	<i>Gymnopilus spectabilis</i>	Mushroom	methanolic extract	GC/MS	southern Western Ghats, India	V. Ragupathi <i>et al.</i> , 2018 [75]

## Continued

Hexamethylcyclotrisiloxane (D3,4)	<i>Bacillus subtilis</i> strain Bs-1	Hay bacillus (Gram-positive bacterium)	Volatile organic compounds	GC/MS	Laboratory in China	H. Cao <i>et al.</i> , 2019 [76]
Hexamethylcyclotrisiloxane (D3,4)	<i>Punica granatum</i>	Pomegranate	fruit rind		Supermarket bought, Vellore Institute of Technology, Vellore campus	A. Prakash and V. Suneetha, 2014 [77]
Hexamethylcyclotrisiloxane (D3,4)	<i>Dillenia scabrella</i>	(Deciduous tree)	leaf (methanolic extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
Hexamethylcyclotrisiloxane (D3,4)	<i>Caesalpinia bonducella</i>	Knicker nut	seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi <i>et al.</i> 2020 [79]
Hexamethylcyclotrisiloxane (D3,4)	<i>Bidens pilosa</i>	black-jack (Asteraceae)	leaf (aqueous ethanolic extract)	GC/MS	University of Fort Hare farm, South Africa	A.B. Falowo <i>et al.</i> , 2017 [80]
Hexamethylcyclotrisiloxane (D3,4)	<i>Dillenia scabrella</i>	(deciduous tree)	leaf (ethanolic – ethyl acetate extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
Hexamethylcyclotrisiloxane (D3,4)	<i>Dillenia scabrella</i>	(deciduous tree)	bark (ethanolic – ethyl acetate extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
Hexamethylcyclotrisiloxane (D3,4)	<i>Cinnamomum camphora</i>	camphor tree (evergreen tree)	leaf (methanolic extract)	GC/MS	Central South University of Forestry and Technology, P. R. China	N.-C. Li <i>et al.</i> , 2015 [81]
Hexamethylcyclotrisiloxane (D3,4)	<i>Andrographis echinoides</i>	False water willow (Acanthaceae)	Leaf	GC/MS	Sengippatti, Tamil Nadu, India	K. Jeevanantham and A. Zahir Hussain, 2018 [82]
Hexamethylcyclotrisiloxane (D3,4)	<i>Abrus precatorius</i>	jequirity bean/rosary pea		GC/MS		Hussain and Kumaresan, 2014 [83]

## Continued

Hexamethylcyclotrisiloxane (D3,4)	<i>Rumex nervosus</i>	Nerveleaf dock	Methanolic leaf extract Extraction was performed at King Saud University	GC/MS	Bait, Al-Radmah district, Ibb governorate, Yemen	M.M. Azzam <i>et al.</i> , 2020 [84]
Hexamethylcyclotrisiloxane (D3,4)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
Hexamethylcyclotrisiloxane (D3,4)	<i>Blighia unijugata</i> Baker	Triangle-tops evergreen tree (Sapindaceae)	essential oil (stem and flowers)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
Octamethylcyclotetrasiloxane (D4,5)	<i>Phyllostachys heterocyclus</i> ( <i>Phyllostachys edulis</i> )	Bamboo	Biomass	GC/MS	China	Q.Z. Ma <i>et al.</i> , 2010 [71]
Octamethylcyclotetrasiloxane (D4,5)	<i>Drypetes hainanensis</i>	Putranjivaceae	Leaf and branch	GC/MS	China	P.H. Liu <i>et al.</i> , 2013 [87]
Octamethylcyclotetrasiloxane (D4,5)	<i>Pistia stratiotes</i>	Water lettuce (Araceae)	Root exudates (hydroponic experiments – nutrients with different phosphorus content)	GC/MS	China	J. Zhang <i>et al.</i> 2019 [88]
Octamethylcyclotetrasiloxane (D4,5)	<i>Piper betle</i>	Betel (Piperaceae)	Leaf	GC/MS	Nanjikkottai, Thanjavur Dt. Tamilnadu, India	F.F.S. Beatrice and G. Santhi, 2017 [89]
Octamethylcyclotetrasiloxane (D4,5)	<i>Bacillus subtilis</i> strain Bs-1	Hay bacillus (Gram-positive bacterium)	Volatile organic compounds	GC/MS	Laboratory in China	H. Cao <i>et al.</i> , 2019 [76]
Octamethylcyclotetrasiloxane (D4,5)	<i>Dillenia scabrella</i>	(deciduous tree)	leaf (methanolic extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
Octamethylcyclotetrasiloxane (D4,5)	<i>Dillenia scabrella</i>	(deciduous tree)	leaf (ethanolic – ethyl acetate extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
Octamethylcyclotetrasiloxane (D4,5)	<i>Dillenia scabrella</i>	(deciduous tree)	bark (methanolic extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]

## Continued

Octamethylcyclotetrasiloxane (D4,5)	<i>Camellia oleifera</i> Abel.	Tea oil camellia	seed (oil)	GC/MS	Zengcheng Teaching and Research Bases, South China Agricultural University, China	J. He <i>et al.</i> , 2021 [90]
Decamethylcyclopentasiloxane (D5,6)	<i>Brassica oleracea</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
Decamethylcyclopentasiloxane (D5,6)	<i>Hirsutella sinensis</i>	Caterpillar fungus (Ophiocordycipitaceae)		GC/MS		S. Yu <i>et al.</i> , 2012 [92]
Decamethylcyclopentasiloxane (D5,6)	<i>Elaeis guineensis</i>	Oil palm	Palm leaf extract	GC/MS	Ughelli, Delta State, Nigeria	P. Onakurhfe <i>et al.</i> 2019 [93]
Decamethylcyclopentasiloxane (D5,6)	<i>Bacillus subtilis</i> strain Bs-1	Hay bacillus (Gram-positive bacterium)	Volatile organic compounds	GC/MS	Laboratory in China	H. Cao <i>et al.</i> , 2019 [76]
Decamethylcyclopentasiloxane (D5,6)	<i>Artemisia vulgaris</i> L.	Mugwort	Essential oil	GC/MS	Tangyin, Henan province, China	Z. Jiang <i>et al.</i> , 2019 [94]
Decamethylcyclopentasiloxane (D5,6)	<i>Juglans regia</i>	walnut	green husks	GC/MS	West Anatolia, Turkey	D. Keskin <i>et al.</i> , 2012 [70]
Decamethylcyclopentasiloxane (D5,6)	<i>Drypetes hainanensis</i>	Putranjivaceae	Leaf and branch	GC/MS	China	P.H. Liu <i>et al.</i> , 2013 [87]
Decamethylcyclopentasiloxane (D5,6)	<i>Bacillus atro-phaeus</i> strain HAB-5	black-pigmented bacteria	from healthy rhizosphere of cotton plant	GC/MS	Xinjiang province, China	M.J.N. Rajaofera <i>et al.</i> , 2019 [95]
Decamethylcyclopentasiloxane (D5,6)	<i>Nigrospora sphaerica</i>	endophytic filamentous fungus of Parthenium hysterophorus		GC/MS	Panjab University, Chandigarh, India	I.B. Prasher and R.K. Dhanda, 2017 [96]
Decamethylcyclopentasiloxane (D5,6)	<i>Pistia stratiotes</i>	Water lettuce (Araceae)	Root exudates (hydroponic experiments – nutrients with different phosphorus content)	GC/MS	China	J. Zhang <i>et al.</i> 2019 [88]
Decamethylcyclopentasiloxane (D5,6)	<i>Polygonatum cirrhifolium</i> (Wall.) Royle	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]

## Continued

Decamethylcyclopentasiloxane (D5,6)	<i>Brainea insignis</i> (Hook.) J. Sm.	Fern (Blechnaceae)	Xylem caudex (stem)	GC/MS	China	Y.N. Fan <i>et al.</i> , 2008 [98]
Decamethylcyclopentasiloxane (D5,6)	<i>Piper betle</i>	Betel (Piperaceae)	Leaf	GC/MS	Nanjikkottai, Thanjavur Dt. Tamilnadu, India	F.F.S. Beatrice and G. Santhi, 2017 [89]
Decamethylcyclopentasiloxane (D5,6)	<i>Phyllostachys heterocyclus</i> ( <i>Phyllostachys edulis</i> )	bamboo	biomass	GC/MS	China	Q.Z. Ma <i>et al.</i> , 2010 [71]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Brassica oleracea</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Bacillus atro-phaeus</i> strain HAB-5	black-pigmented bacteria	from healthy rhizosphere of cotton plant	GC/MS	Xinjiang province, China	M.J.N. Rajaofera <i>et al.</i> , 2019 [95]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Streptomyces</i> sp. strain ND7a	marine bacterium isolated from a sponge		GC/MS	Ha Tien Sea, Kien Giang province, Vietnam	T.V. Phuong <i>et al.</i> , 2018 [99]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Brainea insignis</i> (Hook.) J. Sm.	Fern (Blechnaceae)	Xylem caudex (stem)	GC/MS	China	Y.N. Fan <i>et al.</i> , 2008 [98]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Artemisia vulgaris</i> L.	Mugwort	Essential oil	GC/MS	Tangyin, Henan province, China	Z. Jiang <i>et al.</i> , 2019 [94]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Nigrospora sphaerica</i>	endophytic filamentous fungus of Parthenium hysterophorus		GC/MS	Panjab University, Chandigarh, India	I.B. Prasher and R.K. Dhanda, 2017 [96]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Rosa sterilis</i>		Volatile oil	GC/MS	China	X.Q. Wu <i>et al.</i> , 2014 [100]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Cymbidium faberi</i>	Orchid	Volatiles (related to flower fragrance)	GC/MS	Dangyang, Hubei province, China	Y. Zhou <i>et al.</i> , 2018 [101]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Drypetes hainanensis</i>	Putranjivaceae	Leaf and branch	GC/MS	China	P.H. Liu <i>et al.</i> , 2013 [87]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Polygonatum cirrhifolium</i> (Wall.) Royle	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Hirsutella sinensis</i>	Caterpillar fungus (Ophiocordycipitaceae)		GC/MS		S. Yu <i>et al.</i> , 2012 [92]

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Dodecamethylcyclohexasiloxane (D6,7)	<i>Syzygium cumini</i>	black plum	Seed powder	GC/MS	Aurangabad city, Maharashtra, India	A.H. Abdul Jaleel <i>et al.</i> , 2014 [102]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Argemone ochroleuca</i> Sweet	Mexican poppy (Papaveraceae)	Latex	GC/MS	Abha City, Aseer Region, Saudi Arabia	M.M. Moustafa <i>et al.</i> , 2013 [103]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Pistia stratiotes</i>	Water lettuce (Araceae)	Root exudates (hydroponic experiments – nutrients with different phosphorus content)	GC/MS	China	J. Zhang <i>et al.</i> 2019 [88]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Amaranthus viridis</i> Linn.	Green amaranth (Amaranthaceae)	Leaf	GC/MS	Hyderabad, Telangana, India	D.D. Suneetha <i>et al.</i> , 2017 [104]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Piper betle</i>	Betel (Piperaceae)	Leaf	GC/MS	Nanjikkottai, Thanjavur Dt. Tamilnadu, India	F.F.S. Beatrice and G. Santhi, 2017 [89]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Lycium ruthenicum</i>	Russian ox thorn (Solanaceae)	Volatile oil	GC/MS	China	X. Zhao and K. Li, 2016 [105]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Bacillus subtilis</i> strain Bs-1	Hay bacillus (Gram-positive bacterium)	Volatile organic compounds	GC/MS	Laboratory in China	H. Cao <i>et al.</i> , 2019 [76]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Irpex lacteus</i>	White-rot fungus		GC/MS	Kasauli, Himachal Pradesh, India	R. Chaudhary and A. Tripathy, 2015 [106]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Koeleruteria paniculata</i>	Golden rain tree (Sapindaceae)	Leaves	GC/MS	Iran	S. Ghahari <i>et al.</i> , 2015 [107]
Dodecamethylcyclohexasiloxane (D6,7)	<i>Linum usitatissimum</i>	Flax		GC/MS	India	N. Kaur <i>et al.</i> , 2017 [108]
Tetradecamethylcycloheptasiloxane (D7,8)	<i>Brassica oleraceae</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
Tetradecamethylcycloheptasiloxane (D7,8)	<i>Bacillus cereus</i> S1	Gram positive bacteria isolated from the surface of shrimps	Filtrate	GC/MS	Egypt	S.W.M. Hassan, 2016 [109]

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Tetradecamethylcycloheptas iloxane (D7,8)	<i>Streptomyces</i> <i>sp. strain ND7a</i>	marine bacterium isolated from a sponge		GC/MS	Ha Tien Sea, Kien Giang province, Vietnam	T.V. Phuong <i>et al.</i> , 2018 [99]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Nigrospora</i> <i>sphaerica</i>	endophytic filamentous fungus of Parthenium hysterophorous		GC/MS	Panjab University, Chandigarh, India	I.B. Prasher and R.K. Dhanda, 2017 [96]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Syzygium</i> <i>cumini</i>	Black plum	Seed powder	GC/MS	Aurangabad city, Maharashtra, India	A.H. Abdul Jaleel <i>et al.</i> , 2014 [102]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Amaranthus</i> <i>viridis</i> Linn.	Green amaranth (Amaranthaceae)	Leaf	GC/MS	Hyderabad, Telangana, India	D.D. Suneetha <i>et al.</i> , 2017 [104]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Pistia stratiotes</i>	Water lettuce (Araceae)	Root exudates (hydroponic experiments – nutrients with different phosphorus content)	GC/MS	China	J. Zhang <i>et al.</i> 2019 [88]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Brainea insignis</i> (Hook.) J. Sm.	Fern (Blechnaceae)	Xylem caudex (stem)	GC/MS	China	Y.N. Fan <i>et</i> <i>al.</i> , 2008 [98]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Polygonatum</i> <i>cirrhifolium</i> (Wall.) Royle	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Argemone</i> <i>ochroleuca</i> Sweet	Mexican poppy (Papaveraceae)	Latex	GC/MS	Abha City, Aseer Region, Saudi Arabia	M.M. Moustafa <i>et</i> <i>al.</i> , 2013 [103]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Piper betle</i>	Betel (Piperaceae)	Leaf	GC/MS	Nanjikkottai, Thanjavur Dt. Tamilnadu, India	F.F.S. Beatrice and G. Santhi, 2017 [89]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Irpex lacteus</i>	White-rot fungus		GC/MS	Kasauli, Himachal Pradesh, India	R. Chaudhary and A. Tripathy, 2015 [106]
Tetradecamethylcycloheptas iloxane (D7,8)	<i>Dillenia</i> <i>scabrella</i>	(deciduous tree)	leaf (ethanolic – ethyl acetate extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]

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Hexadecamethylcyclooctasil oxane (D8,15)	<i>Bacillus atro-phaeus strain HAB-5</i>	Black-pigmented bacteria	from healthy rhizosphere of cotton plant	GC/MS	Xinjiang province, China	M.J.N. Rajaofera <i>et al.</i> , 2019 [95]
Hexadecamethylcyclooctasil oxane (D8,15)	<i>Nigrospora sphaerica</i>	Endophytic filamentous fungus of Parthenium hysterophorous		GC/MS	Panjab University, Chandigarh, India	I.B. Prasher and R.K. Dhanda, 2017 [96]
Hexadecamethylcyclooctasil oxane (D8,15)	<i>Polygonatum cirrhifolium (Wall.) Royle</i>	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]
Hexadecamethylcyclooctasil oxane (D8,15)	<i>Cymbidium faberi</i>	Orchid	Volatiles (related to flower fragrance)	GC/MS	Dangyang, Hubei province, China	Y. Zhou <i>et al.</i> , 2018 [101]
Hexadecamethylcyclooctasil oxane (D8,15)	<i>Moschus moschiferus</i>	Musk of musk deer	volatile components of mother tinctures	GC/MS	Russia	Ya.F. Kopytko and N.S. Tsibulko, 2019 [110]
Hexadecamethylcyclooctasil oxane (D8,15)	<i>Hemigraphis colorata (Hemigraphis alternata)</i>	Red ivy (Acanthaceae)	Leaf and stem	GC/MS	Kerala, India	L. Palakkal <i>et al.</i> , 2019 [111]
Hexadecamethylcyclooctasil oxane (D8,15)	<i>Syzygium cumini</i>	Black plum	Seed powder	GC/MS	Aurangabad city, Maharashtra, India	A.H. Abdul Jaleel <i>et al.</i> , 2014 [102]
Hexadecamethylcyclooctasil oxane (D8,15)	<i>Phyllostachys heterocyclus (Phyllostachys edulis)</i>	Bamboo	biomass	GC/MS	China	Q.Z. Ma <i>et al.</i> , 2010 [71]
Hexadecamethylcyclooctasil oxane (D8,15)	<i>Bacillus cereus</i> S1	Gram positive bacteria isolated from the surface of shrimps	Filtrate	GC/MS	Egypt	S.W.M. Hassan, 2016 [109]
Octadecamethylcyclononasil oxane (D9,16)	<i>Bacillus atro-phaeus strain HAB-5</i>	black-pigmented bacteria	from healthy rhizosphere of cotton plant	GC/MS	Xinjiang province, China	M.J.N. Rajaofera <i>et al.</i> , 2019 [95]
Octadecamethylcyclononasil oxane (D9,16)	<i>Rosa sterilis</i>		Volatile oil	GC/MS	China	X.Q. Wu <i>et al.</i> , 2014 [100]
Octadecamethylcyclononasil oxane (D9,16)	<i>Amaranthus viridis</i> Linn.	Green amaranth (Amaranthaceae)	Leaf	GC/MS	Hyderabad, Telangana, India	D.D. Suneetha <i>et al.</i> , 2017 [104]

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Octadecamethylcyclononasil oxane (D9,16)	<i>Brassica oleraceae</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
Octadecamethylcyclononasil oxane (D9,16)	<i>Nigrospora sphaerica</i>	endophytic filamentous fungus of Parthenium hysterophorus		GC/MS	Panjab University, Chandigarh, India	I.B. Prasher and R.K. Dhanda, 2017 [96]
Octadecamethylcyclononasil oxane (D9,16)	<i>Koelreuteria paniculata</i>	Golden rain tree (Sapindaceae)	Leaves	GC/MS	Iran	S. Ghahari <i>et al.</i> , 2015 [107]
Octadecamethylcyclononasil oxane (D9,16)	<i>Polygonatum cirrhifolium</i> (Wall.) Royle	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]
Octadecamethylcyclononasil oxane (D9,16)	<i>Bacillus cereus</i> S1	Gram positive bacteria isolated from the surface of shrimps	Filtrate	GC/MS	Egypt	S.W.M. Hassan, 2016 [109]
Octadecamethylcyclononasil oxane (D9,16)	<i>Piper betle</i>	Betel (Piperaceae)	leaf	GC/MS	Nanjikkottai, Thanjavur Dt. Tamilnadu, India	F.F.S. Beatrice and G. Santhi, 2017 [89]
Eicosamethylcyclodecasiloxane (D10,17)	<i>Polygonatum cirrhifolium</i> (Wall.) Royle	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]
Eicosamethylcyclodecasiloxane (D10,17)	<i>Nigrospora sphaerica</i>	Endophytic filamentous fungus of Parthenium hysterophorus		GC/MS	Panjab University, Chandigarh, India	I.B. Prasher and R.K. Dhanda, 2017 [96]
Eicosamethylcyclodecasiloxane (D10,17)	<i>Rosa sterilis</i>		Volatile oil	GC/MS	China	X.Q. Wu <i>et al.</i> , 2014 [100]
Tetracosamethylcyclododecasiloxane (D12,18)	<i>Brassica oleraceae</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
1.3.5.7-Tetraethyl-1-ethylbutoxysiloxycyclotetrasiloxane (21)	<i>Brassica oleraceae</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
Octamethyl-trisiloxane (22)	<i>Fritillaria pallidiflora</i>	Siberian fritillary	root exudates			Y. Wang <i>et al.</i> , 2009 [112]

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Decamethyl-tetrasiloxane (10)	<i>Dillenia scabrella</i>	(deciduous tree)	bark (methanolic extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
Decamethyl-tetrasiloxane (10)	<i>Fritillaria pallidiflora</i>	Siberian fritillary	root exudates			Y. Wang <i>et al.</i> , 2009 [112]
Decamethyl-tetrasiloxane (10)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
Decamethyl-tetrasiloxane (10)	<i>Blighia unijugata</i> Baker	Triangle-tops evergreen tree (Sapindaceae)	essential oil (flower)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
Dodecamethylpentasiloxane (9)	<i>Brassica oleraceae</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
Tetradecamethylhexasiloxane (11)	<i>Brassica oleraceae</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
Hexadecamethylheptasiloxane (12)	<i>Brassica oleraceae</i> var. Botrytis	Egyptian cauliflower	leaves, stems (hydrodistillation)	GC/MS	Bayaad el Arab, Beni-Suef, Egypt	M.S. Hifnawy <i>et al.</i> , 2013 [91]
Hexadecamethylheptasiloxane (12)	<i>Piper betle</i>	Betel (Piperaceae)	Leaf	GC/MS	Nanjikkottai, Thanjavur Dt. Tamilnadu, India	F.F.S. Beatrice and G. Santhi, 2017 [89]
Hexadecamethylheptasiloxane (12)	<i>Bacillus cereus</i> S1	Gram positive bacteria isolated from the surface of shrimps	Filtrate	GC/MS	Egypt	S.W.M. Hassan, 2016 [109]
Tetradecamethylheptasiloxane (23)	<i>Moringa oleifera</i>	drumstick tree	leaf (aqueous ethanolic extract)	GC/MS	Moringa South Africa Ltd	A.B. Falowo <i>et al.</i> , 2017 [80]
Tetradecamethylheptasiloxane (23)	<i>Bidens pilosa</i>	black-jack (Asteraceae)	leaf (aqueous ethanolic extract)	GC/MS	University of Fort Hare farm, South Africa	A.B. Falowo <i>et al.</i> , 2017 [80]
Hexadecamethyloctasiloxane (24)	<i>Cymbidium faberi</i>	orchid	Volatiles (related to flower fragrance)	GC/MS	Dangyang, Hubei province, China	Y. Zhou <i>et al.</i> , 2018 [101]
Hexadecamethyloctasiloxane (24)	<i>Nigrospora sphaerica</i>	endophytic filamentous fungus of Parthenium hysterophorus		GC/MS	Panjab University, Chandigarh, India	I.B. Prasher and R.K. Dhanda, 2017 [96]

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Hexadecamethyloctasiloxane (24)	<i>Moringa oleifera</i>	drumstick tree	leaf (aqueous ethanolic extract)	GC/MS	Moringa South Africa Ltd	A.B. Falowo <i>et al.</i> , 2017 [80]
Hexadecamethyloctasiloxane (24)	<i>Bidens pilosa</i>	black-jack (Asteraceae)	leaf (aqueous ethanolic extract)	GC/MS	University of Fort Hare farm, South Africa	A.B. Falowo <i>et al.</i> , 2017 [80]
Dimethyl-[bis(tridecyloxy)]silane (26)	<i>Polygonatum cirrhifolium</i> (Wall.) Royle	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]
Dimethyl(docosyloxy)-butoxysilane (27)	<i>Polygonatum cirrhifolium</i> (Wall.) Royle	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]
Diethylheptyloxyoctadecyloxy-silane (28)	<i>Polygonatum cirrhifolium</i> (Wall.) Royle	Solomon's seal (flowering plant) (Asparagaceae)		GC/MS	Narkanda, Himachal Pradesh, India	S.K. Singh and A. Patra, 2019 [97]
Heptamethyl-phenyl-cyclotetrasiloxane (20)	<i>Amaranthus viridis</i> Linn.	Green amaranth (Amaranthaceae)	Leaf	GC/MS	Hyderabad, Telangana, India	D.D. Suneetha <i>et al.</i> , 2017 [104]
Nonamethyl-phenyl-cyclopentasiloxane (19)	<i>Amaranthus viridis</i> Linn.	Green amaranth (Amaranthaceae)	leaf	GC/MS	Hyderabad, Telangana, India	D.D. Suneetha <i>et al.</i> , 2017 [104]
3,3-Diisopropoxy-1,1,1,5,5,5-hexamethyltrisiloxane (Diisopropyl bis(trimethylsilyl) orthosilicate) (25)	<i>Andrographis echioides</i>	False water willow (Acanthaceae)	Leaf	GC/MS	Sengippatti, Tamil Nadu, India	K. Jeevanantham and A. Zahir Hussain, 2018 [82]
3,3-Diisopropoxy-1,1,1,5,5,5-hexamethyltrisiloxane (Diisopropyl bis(trimethylsilyl) orthosilicate) (25)	<i>Pteridium aquilinum</i> (L.)	Eagle fern	ethanolic extract	GC/MS	Kanyakumari district, Tamil Nadu, India	R.L.R. Amster and P.P.J. John, 2019 [114]
3,3-Diisopropoxy-1,1,1,5,5,5-hexamethyltrisiloxane (Diisopropyl bis(trimethylsilyl) orthosilicate) (25)	<i>Blighia unijugata</i> Baker	Akpi, triangle-tops evergreen tree (Sapindaceae)	essential oil (flower) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
2-Chloro-6-fluorobenzyl alcohol tert-butyl dimethyl silyl ether (38)	<i>Pteridium aquilinum</i> (L.)	Eagle fern	ethanolic extract	GC/MS	Kanyakumari district, Tamil Nadu, India	R.L.R. Amster and P.P.J. John, 2019 [114]

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2,5-Bis[(trimethylsilyloxy)benzoic acid trimethylsilyl ester (62)	<i>Irpex lacteus</i>	white-rot fungus		GC/MS	Kasauli, Himachal Pradesh, India	R. Chaudhary and A. Tripathy, 2015 [73]
2,5-Bis[(trimethylsilyloxy)benzoic acid trimethylsilyl ester (62)	<i>Zea mays</i>	Sweet corn	Volatile compounds of the corn juice	GC/MS	SICAU76, Sichuan Agricultural University, China	Feng <i>et al.</i> , 2020 [120]
4-Methyl-2-trimethylsilyloxybenzoic acid trimethylsilyl ester (63)	<i>Elaeis guineensis</i>	Oil palm	Palm leaf extract	GC/MS	Ughelli, Delta State, Nigeria	P. Onakurhfe <i>et al.</i> 2019 [93]
Methoxymethyl trimethyl silane (64)	<i>Elaeis guineensis</i>	Oil palm	Palm leaf extract	GC/MS	Ughelli, Delta State, Nigeria	P. Onakurhfe <i>et al.</i> 2019 [90]
1,2-Diphenyltetramethyldisilane (65)	<i>Amaranthus viridis</i> Linn.	Green amaranth (Amaranthaceae)	Leaf	GC/MS	Hyderabad, Telangana, India	D.D. Suneetha <i>et al.</i> , 2017 [104]
3,5-Bis(trimethylsilyl)cyclohepta trienone (41)	<i>Amomum nilgiricum</i>			GC/MS	Western Ghats, India	N. Konappa <i>et al.</i> , 2020 [129]
3,5-Bis(trimethylsilyl)cyclohepta trienone (41)	<i>Dillenia scabrella</i>	(deciduous tree)	leaf (methanolic extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
3,5-Bis(trimethylsilyl)cyclohepta trienone (41)	<i>Psidium guajava</i>	common guava (evergreen shrub/small tree)	Leaf (ethyl acetate extract)	GC/MS	Kerala, India	R.B. Devi <i>et al.</i> , 2018 [131]
3,5-Bis(trimethylsilyl)cyclohepta trienone (41)	<i>Cinnamomum camphora</i>	camphor tree (evergreen tree)	leaf (methanolic extract)	GC/MS	Central South University of Forestry and Technology, P. R. China	N.-C. Li <i>et al.</i> , 2015 [81]
3,5-Bis(trimethylsilyl)cyclohepta trienone (41)	<i>Quercus aliena</i>	Oriental white oak (galcham oak)	Wood	GC/MS	Tongbai Mountain, Henan Province, China	Q.A. Ma <i>et al.</i> , 2015 [171]
3,5-Bis(trimethylsilyl)cyclohepta trienone (41)	<i>Dicranopteris linearis</i>	Old world forked fern	Leaf	GC/MS	Serdang, Selangor, Malaysia	Z. A. Zakaria <i>et al.</i> , 2017 [121]
3,5-Bis(trimethylsilyl)cyclohepta trienone (41)	<i>Andrographis echiooides</i>	False water willow (Acanthaceae)	Leaf	GC/MS	Sengippatti, Tamil Nadu, India	K. Jeevanantham and A. Zahir Hussain, 2018 [82]

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3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Mangifera indica</i>	Mango (Anacardiaceae)	stem bark extract	GC/MS	Dundaye area, Usmanu Danfodiy, Nigeria	H. Sani <i>et al.</i> , 2015 [172]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Smallanthus sonchifolius</i>	yacón		GC/MS		O.V. Demeshko <i>et al.</i> , 2018 [173]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Hylocereus undulatus</i>	dragon fruit	Stem	GC/MS		Q. Ma <i>et al.</i> , 2015 [171]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Punica granatum</i>	pomegranate	fruit rind	GC/MS	Supermarket bought, Vellore Institute of Technology, Vellore campus	A. Prakash and V. Suneetha, 2014 [77]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Microcosmus exasperatus</i> Heller	ascidian	methanolic extract	GC/MS	Tuticorin coast, India	Meenakshi <i>et al.</i> , 2012 [174]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Sargassum wightii</i>	macroalgae	CH <sub>2</sub> Cl <sub>2</sub> extract	GC/MS	South Indian coastal area, Tamil Nadu, India	A.N. Syad <i>et al.</i> , 2013 [175]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Aporosa lindleyana</i> Baill	Flowering plant (Phyllanthaceae)	Ethanol extract of roots	GC/MS	Keeriparai, Kanyakumari District, Tamilnadu, India	S. Ramakrishnan and R. Venkataraman, 2011 [176]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Leea asiatica</i>	Asiatic leea (Vitaceae)	methanolic extract	GC/MS	Andaman and Nicobar Islands, India	S. Ali <i>et al.</i> , 2021 [122]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Fritillaria pallidiflora</i>	Siberian fritillary	root exudates			Y. Wang <i>et al.</i> , 2009 [112]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]
3,5-Bis(trimethylsilyl)cycloheptatrienone (41)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (root)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Zea mays</i>	Sweet corn	Volatile compounds of the corn juice	GC/MS	SICAU76, Sichuan Agricultural University, China	Feng <i>et al.</i> , 2020 [120]

## Continued

1,2-Bis(trimethylsilyl)benzene (2)	<i>Dillenia scabrella</i>	(deciduous tree)	leaf (ethanolic – ethyl acetate extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Solanum nigrum</i>	black nightshade	leaf extract	GC/MS	Elizade University, Ilara-mokin, Ondo state, Nigeria	O.S. Omojokun <i>et al.</i> , 2019 [72]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Dillenia scabrella</i>	(deciduous tree)	leaf (methanolic extract)	GC/MS	West Garo Hills, District of Meghalaya, North East India	K. Momin and S.C. Thomas, 2020 [78]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Cinnamomum camphora</i>	camphor tree (evergreen tree)	leaf (methanolic extract)	GC/MS	Central South University of Forestry and Technology, P. R. China	N.-C. Li <i>et al.</i> , 2015 [81]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Punica granatum</i>	pomegranate	fruit rind	GC/MS	Supermarket bought, Vellore Institute of Technology, Vellore campus	A. Prakash and V. Suneetha, 2014 [77]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Caesalpinia bonducella</i>	Knicker nut	ethanol extract	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Dicranopteris linearis</i>	Old world forked fern	Leaf	GC/MS	Serdang, Selangor, Malaysia	Z. A. Zakaria <i>et al.</i> , 2017 [121]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Andrographis echioides</i>	False water willow (Acanthaceae)	Leaf	GC/MS	Sengippatti, Tamil Nadu, India	K. Jeevanantham and A. Zahir Hussain, 2018 [82]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Elaeis guineensis</i>	Oil palm	Palm leaf extract	GC/MS	Ughelli, Delta State, Nigeria	P. Onakurhefe <i>et al.</i> 2019 [93]

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1,2-Bis(trimethylsilyl)benzene (2)	<i>Camellia oleifera</i> Abel.	Tea oil camellia	seed (oil)	GC/MS	Zengcheng Teaching and Research Bases, South China Agricultural University, China	J. He <i>et al.</i> , 2021 [90]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Leea asiatica</i>	Asiatic leea (Vitaceae)	methanolic extract	GC/MS	Andaman and Nicobar Islands, India	S. Ali <i>et al.</i> , 2021 [122]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Elatostema papillosum</i> Wedd	Nettle plant species (Urticaceae)	methanol extract	GC/MS	Chittagong district, Bangladesh	M.Z. Uddin <i>et al.</i> , 2021 [123]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Azadirachta indica</i>	Neem plant	leaf extract	GC/MS	Ota, Ogun State, Nigeria	D.E. Babatunde <i>et al.</i> , 2019 [124]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Pteridium aquilinum</i> (L.)	Eagle fern	ethanolic extract	GC/MS	Kanyakumari district, Tamil Nadu, India	R.L.R. Amster and P.P.J. John, 2019 [114]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Abrus precatorius</i>	jequirity bean/rosary pea	methanolic extract	GC/MS	Tamil-nadu, India	K. Pavithra <i>et al.</i> , 2020 [125]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Vernonia amygdalina</i>	bitter leaf	leaf extract	GC/MS	Elizade University, Ilara-mokin, Ondo state, Nigeria	O.S. Omojokun <i>et al.</i> , 2019 [72]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Gymnopilus spectabilis</i>	mushroom	methanolic extract	GC/MS	southern Western Ghats, India	V. Ragupathi <i>et al.</i> , 2018 [75]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Bidens pilosa</i>	black-jack (Asteraceae)	leaf (aqueous ethanolic extract)	GC/MS	University of Fort Hare farm, South Africa	A.B. Falowo <i>et al.</i> , 2017 [80]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Syzygium aromaticum</i>	clove	aqueous extract	GC/MS	commercial market, Chennai, Tamil Nadu, India	R.E. Varghese <i>et al.</i> , 2017 [126]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Sesamum indicum</i> L	sesame (Pedaliaceae)	Seeds (light petroleum ether extract)	GC/MS	different states of India	R. Tyagi and V. Sharma, 2014 [73]

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1,2-Bis(trimethylsilyl)benzene (2)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (root)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Berberis vulgaris</i>	Common barbary	inner bark (methanolic extract)	GC/MS	Siahbishe, Chalous, Mazandaran, Iran	S.K. Hosseinihashe mi <i>et al.</i> , 2015 [115]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Rumex nervosus</i>	Nerveleaf dock	Methanolic leaf extract Extraction was performed at King Saud University	GC/MS	Bait, Al-Radmah district, Ibb governorate, Yemen	M.M. Azzam <i>et al.</i> , 2020 [84]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Sceliphron Caementarium</i>	Mud dauber wasp	nest (ethanolic extract)	GC/MS	Coimbatore, Tamil Nadu	P. Susheela <i>et al.</i> , 2018 [127]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Desmodium gangeticum</i>	Shalparni (Fabaceae)	root extract (chloroform)	GC/MS	Herbal garden, Mahatma Gandhi U., Kerala, India	Srivats <i>et al.</i> , 2012 [128]
1,3-Bis(trimethylsilyl)benzene (1)	<i>Dicranopteris linearis</i>	Old world forked fern	Leaf	GC/MS	Serdang, Selangor, Malaysia	Z. A. Zakaria <i>et al.</i> , 2017 [121]
1,3-Bis(trimethylsilyl)benzene (1)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (root) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
1,3-Bis(trimethylsilyl)benzene (1)	<i>Abrus precatorius</i>	jequirity bean/rosary pea	fruit/seeds (steam distillation)	GC/MS		Hussain and Kumaresan, 2014 [83]
1,4-Bis(trimethylsilyl)benzene (3)	<i>Aporosa lindleyana</i> Baill	Flowering plant (Phyllanthaceae)	Ethanolic extract of roots	GC/MS	Keeriparai, Kanyakumari District, Tamilnadu, India	S. Ramakrishnan and R. Venkataraman, 2011 [176]
1,4-Bis(trimethylsilyl)benzene (3)	<i>Fritillaria pallidiflora</i>	Siberian fritillary	root exudates	GC/MS		Y. Wang <i>et al.</i> , 2009 [112]
1,4-Bis(trimethylsilyl)benzene (3)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]

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1,4-Bis(trimethylsilyl)benzene (3)	<i>Azadirachta indica</i>	Neem plant	leaf extract	GC/MS	Ota, Ogun State, Nigeria	D.E. Babatunde <i>et al.</i> , 2019 [124]
1,4-Bis(trimethylsilyl)benzene (3)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]
1,4-Bis(trimethylsilyl)benzene (3)	<i>Vernonia amygdalina</i>	Bitter leaf	leaf extract	GC/MS	Elizade University, Ilara-mokin, Ondo state, Nigeria	O.S. Omojokun <i>et al.</i> , 2019 [72]
5-Methyl-2-trimethylsilyloxy-acetophenone (43)	<i>Bidens pilosa</i>	Black-jack (Asteraceae)	leaf (aqueous ethanolic extract)	GC/MS	University of Fort Hare farm, South Africa	A.B. Falowo <i>et al.</i> , 2017 [80]
5-Methyl-2-trimethylsilyloxy-acetophenone (43)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [78]
5-Methyl-2-trimethylsilyloxy-acetophenone (43)	<i>Dicranopteris linearis</i>	Old world forked fern	Leaf	GC/MS	Serdang, Selangor, Malaysia	Z. A. Zakaria <i>et al.</i> , 2017 [114]
4-Methyl-2-trimethylsilyloxy-acetophenone (42)	<i>Bidens pilosa</i>	Black-jack (Asteraceae)	leaf (aqueous ethanolic extract)	GC/MS	University of Fort Hare farm, South Africa	A.B. Falowo <i>et al.</i> , 2017 [73]
4-Methyl-2-trimethylsilyloxy-acetophenone (42)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
2'-(Trimethylsilyloxy)propionone (44)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]
2'-(Trimethylsilyloxy)propionone (44)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (stem) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
2'-(Trimethylsilyloxy)propionone (44)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
Benzenepropanoic acid tert-butyl dimethylsilyl ester (37)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]

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1,4-Phenylenebis[trimethylsilane] 1,4-Bis(trimethylsilyl)benzene (3)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
Diethyl silicic acid bis (trimethylsilyl) ester (49)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]
Diethyl silicic acid bis (trimethylsilyl) ester (49)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
Diethyl silicic acid bis (trimethylsilyl) ester (49)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
Trimethyl-(4-tert-butylphenoxy)silane (35)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]
Trimethyl-(4-tert-butylphenoxy)silane (35)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
Trimethyl[5-methyl-2-(1-methylethyl) phenoxy]silane (34) (Thymol-TMS)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
Trimethyl[5-methyl-2-(1-methyl ethyl)phenoxy]-silane Thymol-TMS (34)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethanol extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
Trimethyl[4-(1-methyl-1-methoxyethyl)phenoxy]silane (33)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
Trimethyl[4-(1-methyl-1-methoxyethyl)phenoxy]silane (33)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
2-[(tert-Butyldimethylsilyloxy)-1-isopropyl dimethyl-benzene (66)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (stem bark) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]

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2-[(tert-Butyldimethylsilyl)oxy]-1-isopropyl-4-methyl-benzene (39)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (stem bark, stem and root) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
1,2-Bis(trimethylsiloxy)ethane (29)	<i>Berberis vulgaris</i>	Common barbary	inner bark (methanolic extract)	GC/MS	Siahbishe, Chalous, Mazandaran, Iran	S.K. Hosseinihashe mi <i>et al.</i> , 2015 [115]
Trimethyl[5-methyl-2-(1-methylethyl)phenoxy]silane Thymol-TMS (34)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (flower) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
Trimethyl[4-(2-methyl-4-oxo-2-pentyl)phenoxy]silane (45) 4-(4-Hydroxyphenyl)-4-methyl-2-pentanone, TMS derivative	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (stem bark, stem and root) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
Trimethyl[4-(2-methyl-4-oxo-2-pentyl)phenoxy]silane (45) 4-(4-Hydroxyphenyl)-4-methyl-2-pentanone, TMS derivative	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
tert-Butyl-(5-isopropyl-2-methylphenoxy)dimethylsilane (39)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
Diethyl bis(trimethylsilyl)silicate (30)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (flower) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
Methyltris(trimethylsiloxy)silane (31)	<i>Blighia unijugata</i> Baker	triangle-tops evergreen tree (Sapindaceae)	essential oil (stem bark) (steam distillation)	GC/MS	University of Ibadan, Nigeria	D.O. Moronkola <i>et al.</i> , 2017 [86]
Methyltris(trimethylsiloxy)silane (31)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
[(4-Hexylbenzene-1,3-diyl)bis(oxy)]bis(trimethylsilane) (32)	<i>Camellia oleifera</i> Abel.	Tea oil camellia	seed (oil)	GC/MS	Zengcheng Teaching and Research Bases, South China Agricultural University, China	J. He <i>et al.</i> , 2021 [90]

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1-[Dimethyl(phenyl)silyloxy]pentane (56)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
1,2-Bis(trimethylsilyl)glyceryl linoleate (67)	<i>Microcosmus exasperatus</i> Heller	ascidian	methanolic extract	GC/MS	Tuticorin coast, India	Meenakshi <i>et al.</i> , 2012 [174]
1-Trimethylsilyl-2-piperidinecarboxylic acid trimethylsilyl ester (55)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
9 $\alpha$ -Hydroxy-17 $\beta$ -(trimethylsilyloxy)-4-androsten-3-methyloxime (69)	<i>Berberis vulgaris</i>	Common barbary	inner bark (methanolic extract)	GC/MS	Siahbishe, Chalous, Mazandaran, Iran	S.K. Hosseinihashe mi <i>et al.</i> , 2015 [115]
3-Trimethylsilyloxy-androstane-11,17-dione derivative (70)	<i>Sceliphron Caementarium</i>	Mud dauber wasp	nest (ethanolic extract)	GC/MS	Coimbatore, Tamil Nadu	P. Susheela <i>et al.</i> , 2018 [127]
<i>N</i> -( <i>tert</i> -Butyldimethylsilyl)-1,2-benzisothiazol-3-amine (36)	<i>Caesalpinia bonducella</i>	Knicker nut	Seed kernels (ethyl acetate extract)	GC/MS	Kolli hills, Nammakkal District of Tamil Nadu, India	A. Thenmozhi, <i>et al.</i> 2020 [79]
<i>N,N</i> -Dimethyl-4-nitroso-3-(trimethylsilyl)aniline (57)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]
<i>N</i> -[4-(Trimethylsilyl)phenyl]acetamide 4-(Trimethylsilyl)acetanilide (58)	<i>Gardicinia kola</i>	Bitter kola	n-Hexane extracts of seeds	GC/MS	Southwestern Nigeria	Penduka <i>et al.</i> , 2014 [85]

Table 4. List of silylated inorganic compounds isolated from plants.

Name of isolated compound	Latin name of the plant	Common name of the plant	Fraction in which the compound was isolated from	Type of analysis	Location	Reference
Arsenous acid, tris(trimethylsilyl)ester Tris(trimethylsilyloxy)arsane (52)	<i>Bidens pilosa</i>	Black-jack (Asteraceae)	leaf (aqueous ethanolic extract)	GC/MS	University of Fort Hare farm, South Africa	A.B. Falowo <i>et al.</i> , 2017 [80]
Arsenous acid, tris(trimethylsilyl)ester Tris(trimethylsilyloxy)arsane (52)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]

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Arsenous acid, tris(tert-butylsilyl)ester Tris(tert-butyl)dimethylsilyloxy)arsane (53)	<i>Bidens pilosa</i>	Black-jack (Asteraceae)	leaf (aqueous ethanolic extract)	GC/MS	University of Fort Hare farm, South Africa	A.B. Falowo <i>et al.</i> , 2017 [80]
Arsenous acid, tris(tert-butyl)dimethylsilyl)ester, tris(tert-butyl)dimethylsilyloxy)arsane (53)	<i>Momordica cymbalaria</i> Hook. F.	Karchikai - Vine (Cucurbitaceae)	methanolic extract of the tuber	GC/MS	Sattur Taluk, Virudhunager District, Tamil Nadu, India	M. Gurusamy <i>et al.</i> , 2019 [74]

**Table 5.** List of silylated inorganic compounds isolated from processed plant parts, including in fermented food.

Name of isolated compound	Latin name of the plant	Common name of the plant and type of processing	Fraction in which the compound was isolated from	Type of analysis	Location	Reference
Hexamethylcyclotrisiloxane (D3,4)	<i>Amorphophallus paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]
Hexamethylcyclotrisiloxane (D3,4)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
Octamethylcyclotetrasiloxane (D4,5)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
Decamethylcyclopentasiloxane (D5,6)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
Tetradecamethylcycloheptasiloxane (D7,8)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]

## Continued

Octadecamethylcyclononasiloxane (D9,16)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
Decamethyltetrasiloxane (10)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
[[4-[1,2-Bis(trimethylsilyloxy)ethyl]-1,2-phenylene]bis(oxy)]bis(trimethylsilyl)silane (71)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
1,1,1,3,5,5,5-Heptomethyltrisiloxane (72)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
Diethyl silicic acid bis(trimethylsilyl) ester (49) Diethyl silicic acid bis(trimethylsilyl) ester	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
Methyltris(trimethylsiloxy)silane (31)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
Fluorotrimethylsilane (trimethylsilyl fluoride) (61)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
1,2-Bis(trimethylsilyl)benzene (2)	<i>Amorphophallus paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]

## Continued

1,3-Bis(trimethylsilyl)benzene (1)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
1,4-Bis(trimethylsilyl)benzene (3)	<i>Lonicera edulis</i>	Haskap or honeyberry (fermented <i>Saccharomyces cerevisiae</i> )	volatiles	GC/MS	Heilongjiang Daxinganling Beyond Wild Berries Development Co. Ltd.	Yang <i>et al.</i> , 2018 [116]
1,4-Bis(trimethylsilyl)benzene (3)	<i>Amorphophalla paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]
Trimethyl[4-(2-methyl-4-oxo-2-pentyl)phenoxy]silane (45) 4-(4-Hydroxyphenyl)-4-methyl-2-pentanone, TMS derivative	<i>Amorphophalla paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]
5-Methyl-2-trimethylsilyloxyacetophenone (43)	<i>Amorphophalla paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]
<i>N</i> -( <i>tert</i> -Butyldimethylsilyl)-1,2-benzisothiazol-3-amine (36)	<i>Amorphophalla paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]
Dimethyldecyloxyhexadecyloxysilane (73)	<i>Amorphophalla paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]
Silicic acid diethyl bis(trimethylsilyl)ester (49)	<i>Amorphophalla paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]

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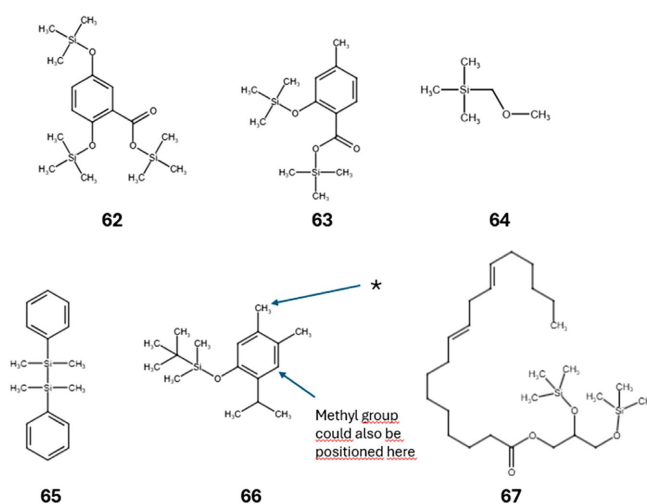
Arsenous acid, tris(tert-butylsilyl)ester Tris(tert-butyl)dimethylsilyloxy)arsane (53)	<i>Amorphophallus paeoniifolius</i>	Elephant foot yam roots and tubers (fermented with probiotic <i>Lactobacillus plantarum</i> )	volatiles	GC/MS	Raipur, Chhattisgarh, India	S.S. Behera <i>et al.</i> , 2019 [132]
Hexamethylcyclotrisiloxane (D3,4)	<i>Camellia sinensis var. kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China	Gong <i>et al.</i> 2012 [177]
Octamethylcyclotetrasiloxane (D4,5)	<i>Camellia sinensis var. kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China	Gong <i>et al.</i> 2012 [177]
Decamethylcyclopentasiloxane (D5,6)	<i>Camellia sinensis var. kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China	Gong <i>et al.</i> 2012 [177]
Tetradecamethylheptasiloxane (23)	<i>Camellia sinensis var. kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China	Gong <i>et al.</i> 2012 [177]
4-(Trimethylsilyl)acetanilide (58) ( <i>N</i> -[4-(Trimethylsilyl)phenyl]acetamide)	<i>Camellia sinensis var. kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China	Gong <i>et al.</i> 2012 [177]

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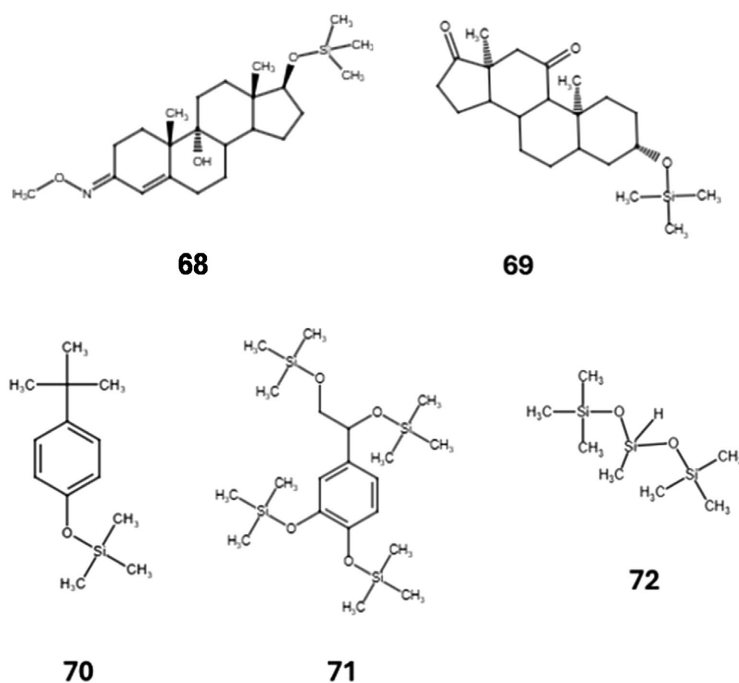
[4-(1,1-Dimethylethylphenoxy)trimethylsilyl]silane ( <b>35</b> ) Trimethyl-(4-tert-butylphenoxy)silane	<i>Camellia sinensis</i> var. <i>kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China	Gong <i>et al.</i> 2012 [177]
3,3-Diethoxy-1,1,1,5,5,5-hexamethyltrisloxane ( <b>49</b> )	<i>Camellia sinensis</i> var. <i>kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China	Gong <i>et al.</i> 2012 [177]
1,2-Bis(trimethylsilyl)benzene ( <b>2</b> )	<i>Camellia sinensis</i> var. <i>kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China	Gong <i>et al.</i> 2012 [177]
[(tert-Butyldimethylsilyloxy)benzene ( <b>74</b> )	<i>Camellia sinensis</i> var. <i>kitamura</i>	Theabrownins from fermented green Zijuan tea	Volatiles gained from pyrolysis of theabrownins	CP-Py-GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China SICAU76, Sichuan Agricultural University, China	Gong <i>et al.</i> 2012 [177]
[[4-[1,2-Bis(trimethylsilyloxy)ethyl]-1,2-phenylene]bis(oxy)]bis(trimethylsilyl)silane ( <b>71</b> )	<i>Zea mays</i>	Sweet corn	Volatile compounds of the corn juice	GC/MS	SICAU76, Sichuan Agricultural University, China	Feng <i>et al.</i> , 2020 [120]
2,5-Bis(trimethylsilyloxy)benzaldehyde ( <b>47</b> )	<i>Zea mays</i>	Sweet corn	Volatile compounds of the corn juice	GC/MS	SICAU76, Sichuan Agricultural University, China Zengcheng Teaching and Research Bases, South China Agricultural University, China	Feng <i>et al.</i> , 2020 [120]
3-Chloropropane-1,2-diol, bis(tert-butyltrimethylsilyl) ether ( <b>40</b> )	<i>Camellia oleifera</i> Abel.	Tea oil camellia	Roasted seed (oil)	GC/MS	Yunnan Tea Research Institute of Yunnan Academy of Agricultural Sciences, China Zengcheng Teaching and Research Bases, South China Agricultural University, China	J. He <i>et al.</i> , 2021 [90]

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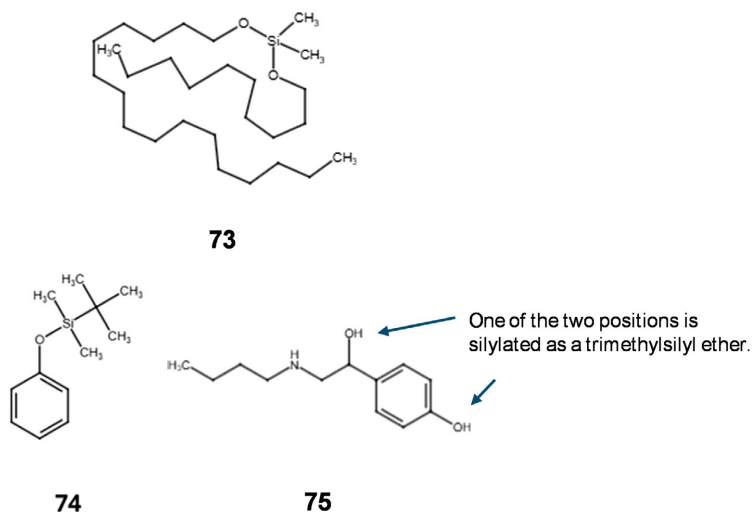
Octamethylcyclotetrasiloxane (D4, 5)	<i>Camellia oleifera</i> Abel.	Tea oil camellia	Fried and steamed seed (oil)	GC/MS	Zengcheng Teaching and Research Bases, South China Agricultural University, China	J. He <i>et al.</i> , 2021 [90]
1,2- Bis(trimethylsilyl)benzene (2)	<i>Camellia oleifera</i> Abel.	Tea oil camellia	Steamed seed (oil)	GC/MS	Zengcheng Teaching and Research Bases, South China Agricultural University, China	J. He <i>et al.</i> , 2021 [90]
[(4-Hexylbenzene-1,3-diyl)bis(oxy)]bis(trimethylsilane) (32)	<i>Camellia oleifera</i> Abel.	Tea oil camellia	Steamed seed (oil)	GC/MS	Zengcheng Teaching and Research Bases, South China Agricultural University, China	J. He <i>et al.</i> , 2021 [90]
Bamethan, TMS derivative (75)	<i>Camellia oleifera</i> Abel.	Tea oil camellia	Roasted seed (oil)	GC/MS	Zengcheng Teaching and Research Bases, South China Agricultural University, China	J. He <i>et al.</i> , 2021 [90]



**Figure 19.** Structures of compounds found in the tables, but not specifically discussed in the text (I).



**Figure 20.** Structures of compounds found in the tables, but not specifically discussed in the text (II).



**Figure 21.** Structures of compounds found in the tables, but not specifically discussed in the text (III).

#### 4. Conclusions

Both siloxanes and alkyl-/arylsilanes have been isolated from plant extracts as well as from other organisms such as fungi and bacteria. The relative frequency with which the different compounds are reported reflects their usage volume and anthropogenic emissions, with medium ring sized permethylated cyclosiloxanes being the most often noted compounds. This makes it highly likely that most if not all of the compounds that have been reported are of anthropogenic origin rather

than natural metabolites. Under certain conditions, it is known that both septa bleed and column bleed fragments appear as ghost peaks in gas chromatography, where again medium ring sized permethylated cyclosiloxanes are typical compounds that are obtained.

Sometimes, extracts are silylated before injection into the gas chromatograph, in order to make the components more volatile. Clearly, this leads to a plethora of silylated compounds, including silylated by-products. If used, this derivatization should always be mentioned in the experimental part of a paper.

Finally, while Si can regulate a number of enzymes *in vivo*, the exact molecular mechanism of Si with these enzymes is still poorly understood. Although no silylated compounds have yet been unequivocally identified as metabolites in plants or other organisms, confirming their existence would be highly intriguing. Advancing our understanding of how silicon interacts with proteins at the molecular level, along with the continued search for definitive evidence of silicon-containing metabolites, remains invaluable.

## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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