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SYSTEMATIC REVIEW

Isolation of Phthalates and Terephthalates from Plant Material – Natural Products or Contaminants?

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Abstract:

Dialkyl phthalates have been used as plasticizers in polymers for decades. As mobile, small weight molecules, phthalates have entered the environment, where they have become ubiquitous. On the other hand, phthalates continue to be isolated from natural sources, plants, bacteria and fungi as *bona fide* natural products. Here, doubt remains as to whether the phthalates represent actual natural products or whether they should all be seen as contaminants of anthropogenic origin. The following article will review the material as presented in the literature.

Keywords : Phthalates, Natural product isolation, Contamination, Terephthalates, Pesticides, Agriculture.

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1. INTRODUCTION

Phthalates are ubiquitous compounds that have been used as plasticizers in polymers for many decades, starting in the late 1920s – early 1930s, where a number of patents showed the rising interest in these products at the time [1, 2] and where phthalates started to replace camphor-based plasticizers. Phthalates have been especially associated with the emergence of plastics such as polyvinyl chloride [3]. At the same time, phthalates, many of which are environmentally quite mobile, have become pervasive pollutants of our biosphere, entering both water and soil. Although especially the low-MW phthalates can be readily degraded hydrolytically [4], photochemically [5] and microbially [6], detectable amounts of phthalates can be found almost everywhere, including in our diet [7]. Low-MW phthalates are dermally absorbed relatively easily. This leads to the identification of phthalates and phthalate derivatives in humans, easily detectable in urine [8], breast milk [9], and blood [10]. It has been found that the concentrations of phthalates in the air are often higher in urban than in rural areas [11, 12]. Nevertheless, phthalates have been identified in soil, for instance, as leachates from plastic mulching/plastic film greenhouses [13, 14], and also because they are used as agricultural adjuvants in pesticides [15] (Fig. **1**).

Phthalates have been isolated from many plants, from algae, bacteria and fungi. In the natural product isolations, oftentimes, the phthalates were looked upon as plant secondary metabolites. As often is the case, after isolation of the products from the plant, the bioactivity of the compounds was studied. In regard to the phthalates, multiple researchers have remarked on various biological activities of the molecules. Intriguing is the comparison of these studies and the investigations of different governmental organizations on the health effects of phthalates as components of consumer products. Sometimes, there can be a disconnect when scientists in closely related but highly specialized, clearly demarcated research areas do not cross-disseminate their fields with information flow. In the case of the study of phthalates, academically, there seem to be rather different areas of research and development that little overlap and often show little data transfer: the development of new product formulations with phthalates, the analytical detection and quantification of phthalates in our daily products and in our environment, often coupled with the assessment of health implications, the study of the degradation of phthalates by bacteria and other microorganisms and lastly the isolation of phthalates as possible natural products from plants and other organisms. In view of the ubiquity of phthalates in our environment, few research papers on the isolation of phthalates from plants have asked whether these products might not be of anthropogenic origin. Nevertheless, two prior review articles have looked at the possibility that at least some of the isolated phthalates could indeed be natural products [16, 17], with a further essay asking the question of whether medicinal plants are polluted with phthalates [18]. In the current contribution, the author reassesses with the aid of published research articles how far phthalates isolated from organisms are indeed natural

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products or whether they can be seen mostly as contaminants. (Fig. **2**)

1.1. Phthalates – Trends in Production and Usage; Health Concerns

Of the roughly 60 different commercially produced phthalates, there are 26 phthalates that are relatively commonly used. The usage of the most common phthalates is shown in Table **1**. In 2001, the breakdown of use of different types of phthalates in Europe was reported as follows: di(ethylhexyl) phthalate (DEHP, **9**), 51%; diisodecyl phthalate (DIDP), 21%; diisononyl phthalate (DINP, **15**), 11%; dibutyl phthalate (**5**), 2% and others, 17% [19]. At that time, about 8.4 million tons of plasticizer were produced every year. Of DEHP (**9**), 3.0 million tons were produced in 2006 alone. In the late 2010s, many of the C3-C6 phthalates were replaced with higher MW C9-C13 phthalates [20], with DEHP (**9**) still abundantly being produced, but in different parts of the world, more and more being replaced by DINP (**15**). DINP (**15**) as a "high" phthalate has a longer residency time in plastics, which gives the plastics better durability. It must be noted that while oftentimes the higher branched phthalates are produced as a mixture of isomers, only one isomer for each phthalate is shown in the drawings and tables in the article. Overall, from 2010 onwards, non-phthalate plasticizers are increasingly invading the market. These include terephthalates (Fig. **3**), epoxy, trimellitates, and some aliphatics/cycloaliphatics (mainly hydrogenated phthalates such as diisononyl cyclohexane-1,2-dicarboxylate [DINCH] which is a mixture of isomers which includes **44**), alkane α,ω-dicarboxylates such as di(2-ethylhexyl) adipate (DEHA, **49**), and alkane tricarboxylates such as acetyl tri-n-butyl citrate (ATBC, **50**) and biomass-derived triglycerides [21]). The market shares of these are forecasted to grow strongly as they continue to replace phthalates [22]. It is estimated that in 2005, 88% of the plasticizers produced were phthalates. The share of admittedly, a growing market declined to 65% in 2017, and it is predicted to decline even further to about 60% in 2022 [22].

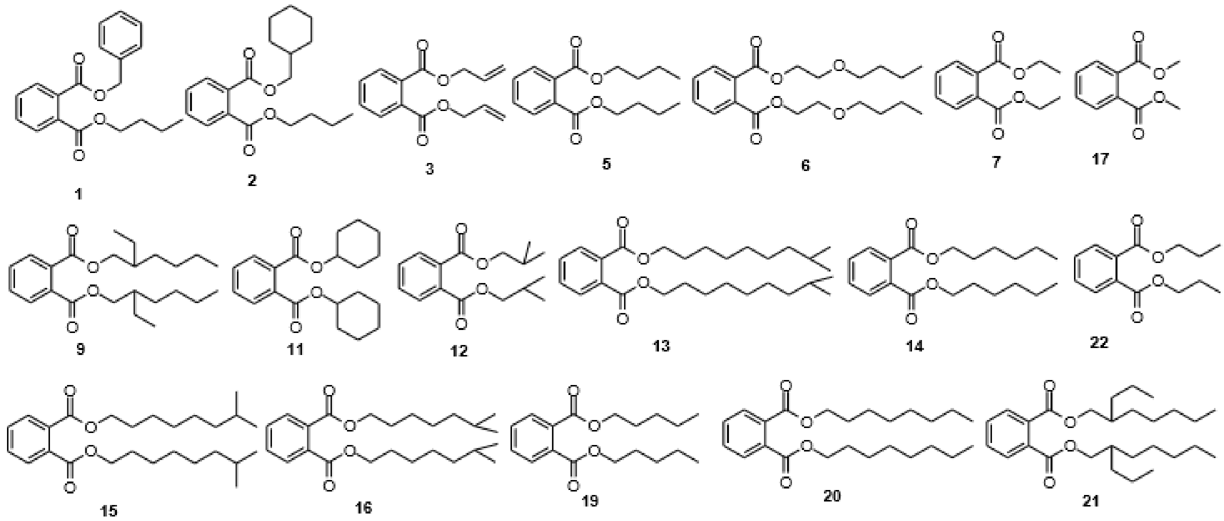

Fig. (1). Structures of some of the industrially most important phthalates.

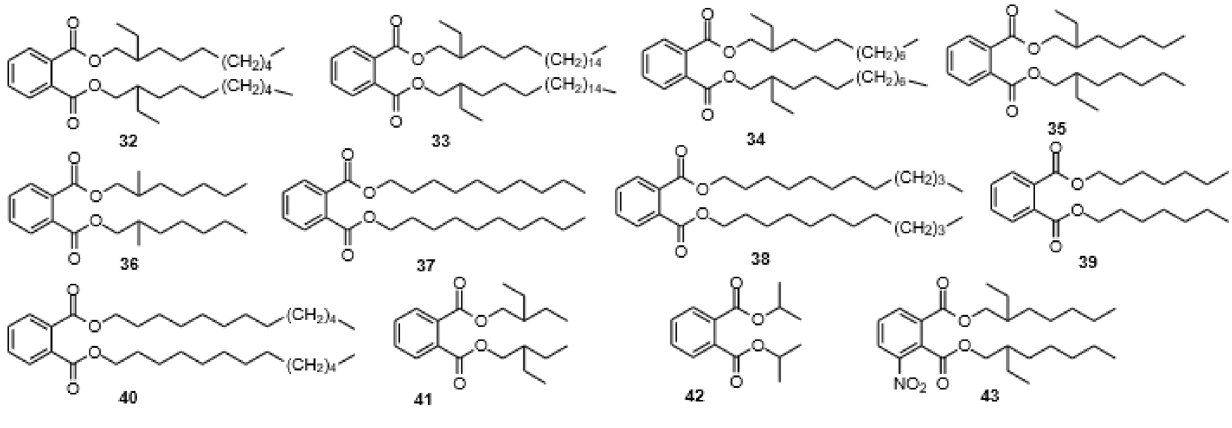

Fig. (2). Phthalates commonly isolated from natural sources.

Table 1. Industrial uses of the most produced phthalates.

Dimethyl phthalate (**17**)	Plasticizer in the production of polyvinyl chloride; coating component in cellulose films; component in laminated safety glasses and shields; as a pesticide (as fermine®); in hair spray (although mostly discontinued in personal care products).
Diethyl phthalate (**7**)	As a fixating agent in fragrances; as excipient and coating material in pharmaceuticals such as in theophylline, erythromycin, verapamil and mianserin formulations.[+]
Dibutyl phthalate (**5**)	Plasticizer in the production of polyvinyl chloride (PVC), polyvinyl acetate (PVA) and rubber; component in latex adhesives, sealants, car care products, solvent and fixative in cosmetics and paints, insecticides, food wrapping materials, as excipient and coating material in pharmaceuticals such as in mesalazine and lithium.[+]
Bis(2-ethylhexyl) phthalate (**9**)	Plasticizer in the production of polyvinyl chloride; plasticizer in toys; clothing, incl. shoes; car upholstery; floor tiles; adhesives and paints; plastic tubings for medical instruments.
Bis(2-propylheptyl) phthalate (**21**)	Plasticizer in PVC.
Benzyl butyl phthalate (**1**)	Plasticizer in the production of polyvinyl chloride, polyurethanes, polysulfides and polyacrylates; vinyl flooring, adhesives, car care products, food wrapping material, and artificial leather.
Diisononyl phthalate (**15**)	Plasticizer in the production of polyvinyl chloride; plasticizer in toys; clothing, incl. shoes; adhesives and paints.
Bis(butoxyethyl) phthalate (**6**)	Plasticizer in PVC and PVA; adhesives.
Diisobutyl phthalate (**12**)	Plasticizer in cellulose nitrate.
Diisodecyl phthalate (**13**)	The coating on furnishings, cookware, coating for pharmaceuticals, food wrapping material.

[+]Z. N. Ennis, S. A. Pedersen, M. R. Hansen, A. Pottegård, T. P. Ahern, J. Hallas, P. Damkier Use of phthalate-containing prescription drugs and the risk of gastric cancer: a Danish nationwide case-control study, *Acta Oncol.*, **2019**, *58*, 852-858.

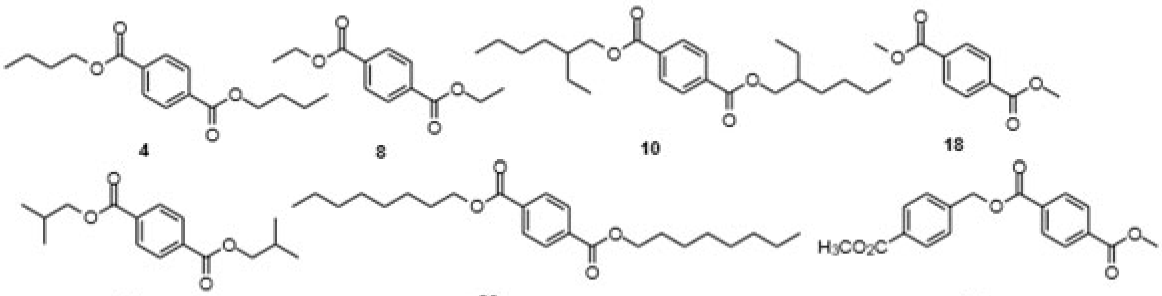

Fig. (3). Terephthalates isolated from natural sources.

This is because of a growing disquiet that phthalates can have harmful effects. DEHP (**9**) has been found to be an endocrine disruptor [23] and possible carcinogen [24], and DINP (**15**) has also been put on the list of possible carcinogens [25] by the California Office of Environmental Health Hazard Assessment (OEHHA) in 2013. In fact, butyl benzyl phthalate (BBzP, **1**), dibutyl phthalate (DnBP, **5**), diethyl phthalate (DEP, **7**), diisobutyl phthalate (DiBP, **12**), diisononyl phthalate (DINP, **15**), di-n-octyl phthalate (DnOP, **20**), dipentyl phthalate (DNPP, **9**), di-isohexyl phthalate, dicyclohexyl phthalate (DcHP, **11**), and di-isoheptyl phthalate have all been associated with illnesses and disorders as diverse as attention-deficit hyperactivity disorder [26], breast cancer [27], obesity [28] and type II diabetes [29], neurodevelopmental issues [30], behavioral issues, autism spectrum disorders [31], altered reproductive development [32] and male fertility issues [33]. It must be said, however, that in many instances, insufficient data is available to make irrefutable statements on the health impacts of phthalates. Some of the compounds replacing phthalates fare a little better. These include the increasingly used terephthalates such as di(2-ethylhexyl) terephthalate. In addition, dimethyl terephthalate (DMT, **18**) which is a starting material in the production of terephthalate based plasticizers as well as in the production of polyalkyl terephthalates [34, 35], especially in the synthesis of polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT), and polybutylene terephthalate (PBT), is looked at as a potential carcinogen and an irritant to skin, eyes and the respiratory tract. As is the case with many monomers and small-molecule starting materials for polymers, also DMT can be found in small concentrations in the respective polymers (Figs. **4** and **5**).

1.2. Phthalates in Agricultural Use – Phthalate Content in Soil and Agricultural Produce

There is extensive literature on phthalate content in agricultural produce, whether it be tomatoes grown after biosolids application [36] or radishes grown with sewage sludge and compost application [37]. Extensive developments in analytical chemistry have led to reliable measurement methods for phthalate contents in different types of produce [38] and in processed and packaged foods [39, 40]. The occurrence of phthalates in agricultural soils around the world [41, 42], with many studies originating in China [43 - 45], has been sufficiently established, where DEHP (**9**) and DnBP (**5**) are the most abundant phthalates found. The use of plastic mulching in agriculture is still a widespread technique to suppress weed growth and to contain water needs. While biodegradable polymeric films have been advertised, the by far most often used material is both high and low-density polyethene (LDPE and HDPE). Phthalates are mulch PE additives, where it has been shown that these phthalates are released partially into the soil [46]. The delivery of phthalates from the plastic film covers of the agricultural plants themselves has been studied in some detail [47]. In addition, sewage sludge [42], agrochemicals [48], wastewater irrigation [49] and the atmosphere [50, 51] itself deliver phthalates to the soil [52 - 54]. Especially, the phthalate uptake of plants from sludge has been a worry [55], where Shea *et al.* [56] reported a di-*n*-butyl phthalate (DnBP, **5**) uptake in corn at 0.32 ppm from soil contaminated with 100 ppm DnBP (**5**). The removal of phthalates from agricultural crop derived extracts designated for food or pharmaceutical use is sometimes seen as a necessity and different processes have been developed to that regard [57].

Phthalates can be cleaved to monophthalates and to phthalic acid by UV light [58], but this is a slow process, at least in water with photochemical half-lives of over 100 days (for butyl benzyl phthalate, **1**), 3 years (for dimethyl phthalate, **17**) and 1000 years [for bis(ethylhexyl)phthalate, **9**] [59, 60]. However, as the phthalates penetrate the soil, the degradation pathway open to them is the aerobic or anaerobic ester hydrolysis with subsequent cleavage of the aromatic ring system [61, 62]. Short-chain phthalates such as diethyl phthalate (DEP, **7**) are degraded more easily by micro-organisms than longer chain phthalates such as bis(2-ethylhexyl) phthalate (DEHP, **9**), which can only be co-metabolically degraded in the presence of an additional carbon source [61, 62]. Different microbial strains have been isolated and used to remove phthalates from different matrices, such as natural water (sea water [63]:), soils [64], sediments [65], wastewater [66], and landfills [67]. A recent review of the microbial degradation of phthalates is available [6].

1.3. Phthalates in Aquatic Environments and Isolated from Marine Produce

Monitoring phthalate concentrations in aquatic environments and in marine products has been going on for a long time. A study from Japan, compares the phthalate level of fish caught in the Uji river in 1973 [68] with fish caught there in 1946! A report from 1986 tells us that in the upper Pickwick reservoirs in north Alabama, USA, phthalates have been found to an appreciable degree in turtles, but not in fish or clams [69].

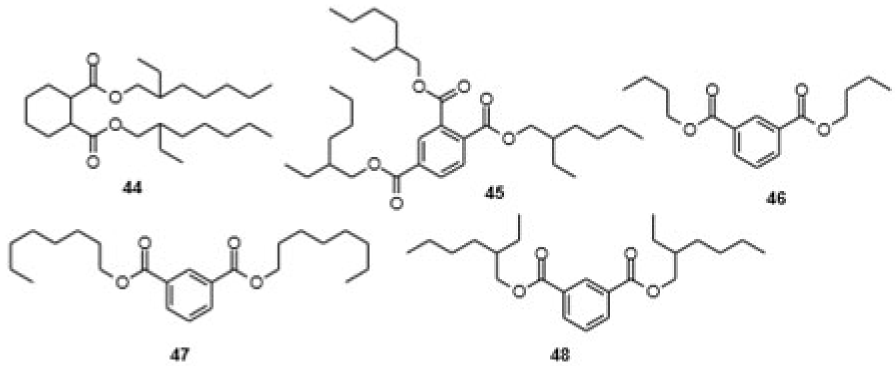

Fig. (4). Isophthalates **46-48**, dinonyl cyclohexane-1,2-dicarboxylate isomer (**44**), and trimellitate **45** as substi-tutes for phthalates as plasticizers.

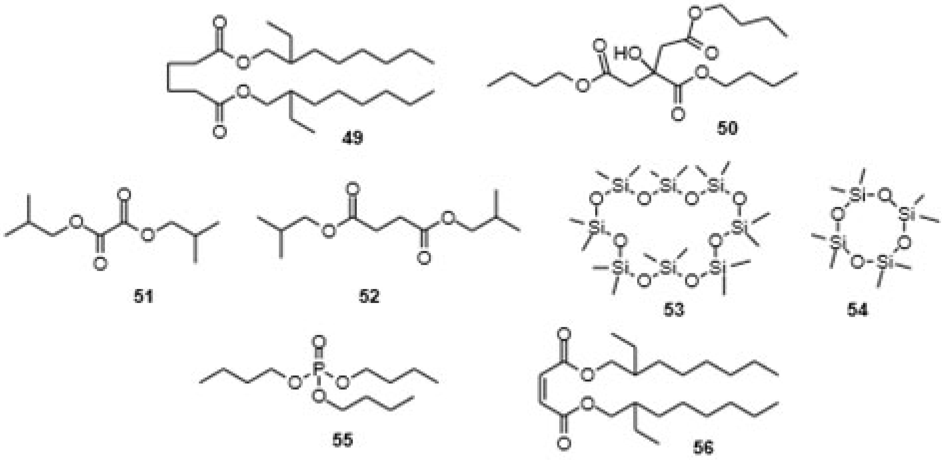

Fig. (5). Dialkyl alkanedioates and alkenedioates **49**, **51**, **52**, and **56**, trialkyl phosphates **55** and cyclosiloxanes **53** and **54**, compounds that often accompany phthalates from natural sources.

A study from Portland, Maine, of 1983 tells us the concentration of dibutyl phthalate (**5**) and di(2-ethylhexyl)phthalate (**9**) in clams were less than those measured in the sediment [70]. A Chinese study from 2003 looked at the concentration of dibutyl phthalate (**5**), diethyl phthalate (**7**) and di(2-ethylhexyl) phthalate (**9**) in water, soil, sediments, and aquatic organisms, including shrimps, fish and clams from Shanghai, Hangzhou Bay, the Grand Canal and surrounding areas [71]. The presence of phthalates in sponges has been explained to have potentially originated from bacteria on the sponges [72].

Meanwhile, there is also beginning to be a good overview of phthalate concentrations in the aquatic environment in different parts of the world, whether it is in the German Bight [73], the Bay of Marseille [74], or the Asan lake in S.-Korea [75]. In addition, the mobility of phthalates and their movement between the atmosphere and water [73, 76] or between sediments and water become more understood. Investigations were carried out with deuterated di-*n*-octylphthalate to better comprehend the uptake of phthalates by mollusks from sediments [77].

Phthalates in marine produce are watched carefully. Thus, phthalate concentrations have been assessed and monitored in commercial marine pelagic fish species such as Atlantic bluefin tuna from Sardinia [9-14.62 ng/g DEHP (**9**); 15.-6.3 ng/g MEHP] [78], Atlantic herring, Atlantic mackerel [17-27 µg/g DIHP (**14**)] [79], Baltic herring [5.6 µg/g DMP (**17**)] and codfish [1.9 µg/g DMP (**17**)] [80]. Phthalate concentrations have also been measured in farmed fish such as in common carp [0.26 mg/kg – 0.72 mg/kg DEHP (**9**), 0.31 mg/kg - 0.56 mg/kg DnBP, (**5**)] [81]. How all this translates to exposure of humans to phthalates is an issue of major concern. Already in 1973, D. Williams noted levels of dibutyl phthalate [**5**, 0-78 ppm] and di(2-ethylhexyl) phthalate [0-160 ppb] in 21 samples of fish available to the Canadian consumer [82]. Since then, a number of studies have looked into the risk of human contact to phthalates through consumption of different types of produce [83 - 86], be it in Belgian, UK, Tunisian or Chinese markets. Overviews of phthalates in food have been published [87].

1.4. Phthalates Isolated from Organisms as Natural Products – Isolation of Phthalate Replacement Products from Organisms

Against this background, there is a large body of literature concerning the isolation of phthalates from organisms as natural products, *i.e.*, not as or not expressly as contaminants found within the organisms (Table **2**). In a number of papers listed here, though, the connection is made between phthalates and plasticizers [88], although it is not precisely noted that the phthalates isolated from the organisms are true of anthropogenic nature. In certain cases, it was not relevant for the authors whether the isolated phthalates were actual plant metabolites or anthropogenic contaminants, such as in the case of identifying the volatile components that make up the bouquet of pineapples of different degrees of ripeness [89], where both dibutyl phthalate (**5**) and diisobutyl phthalate (**12**) were found; or in the case of identifying the flavor components of clams and mussels such as from the Hongdao clam [90], where dibutyl phthalate (**5**) and diethyl phthalate were isolated, or from the muscles of four other Chinese sea clams, where dibutyl phthalate (**5**) and butyl benzyl phthalate (**1**) were isolated [91]. In other cases, the authors were very much aware of the possibility of the isolated phthalate being a contaminant. Thus, Silva *at al*. [92]. were clearly aware that DEHP (**9**) could be a contaminant from laboratory equipment and state that DEHP (**9**) was only isolated from *Diaporthe phaseolorum* and not from other organisms that they worked with under identical conditions. S. E. McKenzie *et al.* isolated bis (2-ethylhexyl) phthalate from the marine fungus *Corollospora lacera*, but showed that the compound was indeed an artifact stemming from the culturing and extraction process [93]. Laboratory contamination with phthalates can happen facilely as the author has also experienced in his laboratory, once both in Japan and in the United Arab Emirates. Typical sources of contamination are solvent bottles made of plastic and cling films. Sources, incidents and remedies of such contaminations have been reviewed by Nguyen *et al.* [94] and Reid *et al.* [95]. Nevertheless, the overwhelming number of reports on the isolation of phthalates from natural organisms originate from the exposure of these organisms to anthropogenic environmental pollution rather than from contamination of the samples in the laboratory. Oftentimes, phthalates are isolated as a bouquet of different phthalates from the organisms [96 - 98], often hand-in-hand with alkanedioates such as diisobutyl oxalate (**51**) and diisobutyl succinate (**52**) in addition to siloxanes such as hexadecamethylcyclooctasiloxane (**53**) and octamethylcyclotetrasiloxane (**54**) that all are known additives in polymers [96]. From the fruits of *Acanthopanax sessiliflorus* (Araliaceae), 13 different phthalates were isolated [99]. In 2020, N. Kumari *et al.* published the isolation of dibutyl phthalate (**5**) as secondary metabolites of an actinomycetes strain grown on actinomycete isolation agar. However, in the same study tert-butylcalix [4] arene, clearly, a synthetic product, was also found as a purported secondary metabolite of the actinomycetes strain [100].

Most of the time, the structures of the phthalates were determined by GC-MS, relying on the retention time of the compounds on the specific column material used and the mass spectrometric data as analyzed by a computer-accessible database. While mostly the data analysis is expected to be correct, such an analysis is not without its danger. Furthermore, isomeric structures, especially of long-chain esters, which in the case of the phthalates are known to be produced industrially oftentimes as isomeric mixtures, are not easily distinguished and need human aided analysis, with multiple mass spectrometric analyses carried out under different conditions. In a number of cases, there is a mismatch between reported and accepted physical data of the phthalates. Thus, DEHP (**9**) has been isolated from *Diaporthe phaseolorum* as a dark yellow solid but resembles a colorless oil [92]. Similarly, di-*n*-butyl phthalate (**5**), isolated as a secondary metabolite of an endophytic fungal strain of *Rumex madaio*, has been reported as a solid, although again, the compound is a colorless oil at room temperature [101]. In many cases, however, extensive NMR spectroscopic analyses bear out the structures of the compounds perfectly.

Table 2. Isolation of dialkyl and monoalkyl phthalates from natural sources (organisms).

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Benzyl phthalate (**24**)	*Hibiscus micranthus*	Malvaceae	root	GC/MS	Telangana, India	K.A. Kumar *et al.*, 2011 [153]
Benzyl butyl phthalate (**1**)	*Astilbe chinensis*	(Saxifragaceae)	volatile oil	GC/MS	China	T. Yang *et al.*, 2011 [96]
Bis(7-acetoxy-2-ethyl-5-methylheptyl) phthalate (**69**)	*Lonicera quinquelocularis*	translucent honeysuckle		IR, ^{1}H NMR, ^{13}C NMR, DEPT, ^{1}H-COSY, HMBC	Pakistan	D. Khan *et al.*, 2014 [133]
Bis(2-butoxyethyl)-phthalate (**6**)	*Launaea arborecsens*	Flowering plant (Asteraceae)	essential oil	GC/MS	Algerian Sahara	A. Cheriti *et al.*, 2006 [154]
Bis (2-methoxycarbonyl-benzoyloxyethyl) ether (**74**)	*Cochliobolus lunatus*	Pathogenic plant fungus		^{1}H NMR	China	M. Chen *et al.*, 2016 [135]
Bis (2-ethylbutyl) phthalate (**41**)	*Calliandra haematocephala Hassk.*	Flowering plant (Fabaceae)	aerial parts	GC/MS	Egypt	A.H.S. Abou Zeid *et al.*, 2006 [155]
Bis(2-ethyldodecyl) phthalate (**34**)	*Hippocampus kuda Bleeler*	seahorse	whole body	IR, HRMS, MS, ^{1}H NMR, ^{13}C NMR	Zhoushan Island, Zhejiang, China	Y. Li *et al.*, 2008 [152]
*Bis(2-ethyleicosyl) phthalate (*33*)*	*Phyllanthus muellerianus*	Evergreen shrub (Euphorbiaceae)			University of Ibadan, Ibadan, Nigeria	M. Saleem *et al.*, 2009 [132]
Bis(2-ethyleicosyl) phthalate (**33**)	*Nepeta kurramensis*	Flowering plant (Lamiaceae)		^{1}H NMR, ^{13}C NMR, 2D-NMR, MS	Khyber Pakhtunkhwa, Pakistan	N. Ur Rehman, 2017 [131]
Bis (2-ethylbutyl) phthalate (**41**)	*Holoptelea integrifolia*	Indian elm	leaf, stem, root	GC/MS	India	A. Kavitha *et al.*, 2014 [195]
Di-isopropyl phthalate (**42**)	*Streptomyces sp.* strain No. A-3315	gram positive bacterium		IR, ^{1}H NMR and ^{13}C NMR	Kumamoto, Japan	M. Uyeda *et al.*, 1990 [148]
Di-isopropyl phthalate (**42**)	*Streptomyces bangladeshensis*	gram positive bacterium (isolated from soil)			Natore, Bangladesh	M.A. Al-Bari *et al.*, 2005 [156]
Bis(2-ethylhexyl) phthalate (**9**)	*Calliandra haematocephala Hassk.*	Flowering plant (Fabaceae)	aerial parts	GC/MS	Egypt	A.H.S. Abou Zeid *et al.*, 2006 [155]
Bis(2-ethylhexyl) phthalate (**9**)	*Bangia atropurpurea*	red algae			Taiwan	C.Y. Chen, 2004 [141]
Bis(2-ethylhexyl) phthalate (**9**)	*Aloe vera*	succulent plant			S.-Korea	K.H. Lee *et al.*, 2000 [157]
Bis(2-ethylhexyl) phthalate (**9**)	*Cryptotaenia canadensis DC.*	Canadian honewort (perennial plant)			Japan	S. Hayashi *et al.*, 1967 [158]
Bis(2-ethylhexyl) phthalate (**9**)	*Penicillium sp.*	Endophytic fungus of *Curcuma zeodaria*		IR, ^{1}H NMR and ^{13}C NMR	South Sumatra, Indonesia	Muharni *et al.*, 2014 [159]
Bis(2-ethylhexyl) phthalate (**9**)	*Calotropis gigantea*	shrub			Rajshahi, Bangladesh	M. Habib and M.R. Karim, 2009 [143] M. Habib and M.R. Karim, 2012 [160]
Bis(2-ethylhexyl) phthalate (**9**)	*Alchornea cordifolia*	shrub	Leaf, root bark		Congo	H. Mavar-Manga *et al.*, 2008 [161]
Bis(2-ethylhexyl) phthalate (**9**)	*Aspergillus fumigatus*	Fungus (isolated from soil samples)		IR, ^{1}H NMR and ^{13}C NMR	Mansoura, Egypt	M.S. Abdel-Aziz *et al.*, 2017 [162]
Bis(2-ethylhexyl) phthalate (**9**)	*Aspergillus awamori*	fungus		^{1}H NMR, ^{13}C NMR, DEPT-Q NMR	Nile river, Egypt	M.M. Lotfy *et al.*, 2018 [163]
Bis(2-ethylhexyl) phthalate (**9**)	*Brevibacterium McBrellneri*	gram-positive actinobacterium		IR, ^{1}H NMR, ^{13}C NMR	India	M. Rajamanikyam *et al.*, 2017 [164]
Bis(2-ethylhexyl) phthalate (**9**)	*Rheinheimera japonica KMM 9513^{T}*	marine bacterium			Sea of Japan	N.I. Kalinovskaya *et al.*, 2017 [165]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Bis(2-ethylhexyl) phthalate (**9**)	*Pseudomonas rhizosphaerae*	marine bacterium			China	S.H. Qi *et al.*, 2009 [166]
Bis(2-ethylhexyl) phthalate (**9**)	*Streptomyces sp.*	Actinomycete (isolated from Saharan soil)		^{1}H NMR, ^{13}C NMR, ^{1}H-^{1}H COSY and ^{1}H-^{13}C HMBC NMR	Ghardaïa, Algeria	E.H. Driche *et al.*, 2015 [167]
Bis(2-ethylhexyl) phthalate (**9**)	*Cinachyrella cavernosa (Lamarck)*	demosponge		GC/MS	Goa, India	S. Wahidullah *et al.*, 2015 [72]
Bis(2-ethylhexyl) phthalate (**9**)	*Caulerpa racemosa* (O. Dargent)	green algae	volatile constituents	GC/MS	Egypt	N.E. Awad, 2002 [168]
Bis(2-ethylhexyl) phthalate (**9**)	*Codium tomentosum* (Stackhouse)	green algae	volatile constituents	GC/MS	Egypt	N.E. Awad, 2002 [168]
Bis(2-ethylhexyl) phthalate (**9**)	*Phyllanthus muellerianus*	Evergreen shrub (Euphorbiaceae)			Pakistan	M. Saleem *et al.*, 2009 [132]
Bis(2-ethylhexyl) phthalate (**9**)	*Lonicera quinquelocularis*	translucent honeysuckle		^{1}H NMR, ^{13}C NMR	Pakistan	D. Khan *et al.*, 2014 [133]
Bis(2-ethylhexyl) phthalate (**9**)	*Nocadia levis*	Actinobacterium (isolated from laterite soil)		IR, MS, ^{1}H NMR, ^{13}C NMR	Guntur, India	A. Kavitha *et al.*, 2009 [97]
Bis(2-ethylhexyl) phthalate (**9**)	*Cladosporium sp.*	Marine fungus (isolated from mangrove stand)			Kei Ling Ha Lo Wai, Sai Kung, Hong Kong, China	S.H. Qi *et al.*, 2009 [166]
Bis(2-ethylhexyl) phthalate (**9**)	*Stoechospermum marginatum (C. agardh) Kuetzing*	brown algae	whole algae		Goa, India	S. Wahidulla, 1995 [169]
Bis(2-ethylhexyl) phthalate (**9**)	*Ligusticum porteri*	Apiaceae	callus, aerial part, root	GC/MS	Chihuahua, Mexico,	D. Goldhaber-Pasillas *et al.*, 2012 [170]
Bis(2-ethylhexyl) phthalate (**9**)	*Ficus carica*	Tunisian caprifig (Moraceae)	Latex of unripe fruit	GC/MS	Mesjed Aissa agricultural field, Tunisia	H. Lazreg-Aref *et al.*, 2012 [171]
Bis(2-ethylhexyl) phthalate (**9**)	*Moringa oleifera*	Drumstick tree (Moringaceae)	leaf		Thanjavur, Tamil Nadu, India	S. Karthika *et al.*, 2013 [172]
Bis(2-ethylhexyl) phthalate (**9**)	*Streptomyces sp. A-3315*	gram positive bacterium	cultural filtrate	IR, ^{1}H NMR, ^{13}C NMR,	Laboratory, Japan	M. Uyeda *et al.*, 1990 [148]
Bis(2-ethylheptyl) phthalate (**35**)	*Hippocampus kuda Bleeler*	seahorse	Whole body	IR, MS, ^{1}H NMR, ^{13}C NMR	Zhoushan Island, Zhejiang, China	Z.J. Qian *et al.*, 2012 [173] Y. Li *et al.*, 2008 [152]
Bis(2-ethylheptyl) phthalate (**35**)	*Bacillus pumilus*	Marine gram-positive bacillus		MS	Bay of Bengal near Andaman and Nicobar islands, India	A.M. Priya, 2012 [174]
Bis(5-ethylheptyl) phthalate (**35**)*	*Nocadia levis*	Actinobacterium (isolated from laterite soil)		IR, MS, ^{1}H NMR, ^{13}C NMR	Guntur, India	A. Kavitha *et al.*, 2009 [97]
Bis(2-ethylheptyl) 3-nitrophthalate (**43**)	*Alstonia boonei*	Deciduous tropical-forest tree	stem bark	GC/MS	Okpuje, Enugu State, Nigeria	A.A. Imam *et al.*, 2017 [175]
Bis(2-ethyldecyl) phthalate (**32**)	*Heliotropium strigosum*	Heliotrope (Boraginacea)	Whole plant material	^{1}H NMR, ^{13}C NMR, MS	Malakand, Pakistan	S.M. Shah *et al.*, 2014 [176]
Bis(2-methylheptyl)-phthalate (**36**)	*Hypericum hyssopifolium*	flowering plant		UV, IR, ^{1}H NMR, ^{13}C NMR, MS, HRMS	Erzurum, Turkey	A. Cakir *et al.*, 2003 [102]
Bis(2-methylheptyl)-phthalate (**36**)	*Phyllanthus pulcher*	Tropical leaf-flower (Phyllanthaceae)			Malaysia	G. Bagalkotkar, 2007 [177]
Bis(2-methylheptyl)-phthalate (**36**)	*Bacillus cereus*	gram-positive bacterium		GC/MS	India	K.M. Anju *et al.*, 2015 [178]
Bis(2-methylheptyl)-phthalate (**36**)	*(marine) Pseudomonas sp.* PB01	gram negative bacterium		^{1}H NMR, ^{13}C NMR, COSY, DEPT, HMBC NMR	GenBank Accession No. EU126129	V.L.T. Hoang *et al.*, 2008 [179]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Bis(2-methylheptyl)-phthalate (**36**)	*Chlorophytum boriviliuanum*	herb	root	^{1}H NMR, ^{13}C NMR, DEPT, COSY, HMBC and HMQC	Malaysia	L.B. Chua *et al.*, 2015 [180]
Bis(2-methylheptyl)-phthalate (**36**)	*Vicia villosa* Roth	hairy vetch (legume)			Gyeongsan, S.-Korea	M.T. Islam *et al.*, 2013 [181]
Bis(2-methylheptyl)-phthalate (**36**)	*Pongamia pinnata*	Evergreen shrub	leaf	IR, ^{1}H NMR, ^{13}C NMR	Chennai, Tamil Nadu, India	P. Rameshthan-gam and P. Ra-masamy, 2007 [182]
Bis(2-methylheptyl)-phthalate (**36**)	*Arundina graminifolia (D. Don) Hochr.*	Bamboo orchid	rhizome	MS, ^{1}H NMR, ^{13}C NMR	China	M. Liu *et al.*, 2007 [183]
Bis(2-methylheptyl)-phthalate (**36**)	*Lantana camara L.*	Perennial shrub	essential oil	GC/MS	China	L. Ren *et al.*, 2016 [184]
Bis(2-methylheptyl)-phthalate (**36**)	*Ponciri fructus (Poncirus trifoliata)*	Trifoliate orange (Rutaceae)	unripen fruit	MS	S.-Korea	A.R. Son *et al.*, 2005 [185] G.-H. Xu *et al.*, 2008 [186]
Bis(2-methylheptyl)-phthalate (**36**)	*Cinnamomi cortex (Cinnamomum cassia Blume)*	Chinese cinnamom (tree)	bark	MS	S.-Korea	H.W. Jung *et al.*, 2007 [187]
Bis(2-methylheptyl)-phthalate (**36**)	*Phellodendri Cortex*	*Phellodendron amurense* Rupr. *Phellodendron chinense* Schneid		MS	S.-Korea	J.G. Lee *et al.*, 2007 [188]
Bis(2-methylheptyl)-phthalate (**36**)	*Sarcophyton glaucum*	Rough leather coral		^{1}H NMR, ^{13}C NMR, 2D-NMR	Sanya Bay, Hainan Island, China	C.X. Zhang *et al.*, 2013 [189]
Bis(2-propylheptyl) phthalate (**21**)	*Flue cured tobacco (Nicotiana)*		Rhizosphere soils of		Mengtong of Shandong province, China	X. Ren *et al.*, 2015 [145]
*Bis (2-[2-hydroxymethyl]nonadec-3(*E*)-enyl)phthalate)* (**68**)	*Nepeta kurramensis*	Flowering plant (Lamiaceae)		^{1}H NMR, ^{13}C NMR, 2D-NMR, MS	Pakistan	N. Ur Rehman *et al.*, 2017 [131]
Bis(3,5,5-trimethylhexyl) phthalate (**98**)	*Alstonia boonei*	Deciduous tropical-forest tree	stem bark	GC/MS	Okpuje, Enugu State, Nigeria	A.A. Imam *et al.*, 2017 [175]
2-Butoxy-2-oxoethyl butyl phthalate (**99**)	*Trichoderma asperellum*	filamentous fungus	cultural filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
n-Butyl phthalate (**25**)	*Desulfovibrio desulfuricans*	marine bacterium (from benthal sea water sample)		^{1}H NMR, ^{13}C NMR	Dalian sea area, China	Y. Zhang *et al.*, 2009 [191]
n-Butyl phthalate (**25**)	*Durian fruit (peel)*	tree	volatile constituents of fruit peel	GC/MS	China	B. Zhang *et al.*, 2012 [192]
n-Butyl phthalate (**25**)	*Fomitiporia punctata*	Fungus (Hymenochaetaceae)	ethanolic extract	GC/MS	China	F. Zhu *et al.*, 2011 [193]
n-Butyl cyclohexyl phthalate (**2**)	*Trichoderma harzianum*	fungus		GC/MS	Nani, Allahabad, and Pipri, Faizabad, India	A. Mishra *et al.*, 2018 [194]
Butyl decyl phthalate (**104**)	*Holoptelea integrifolia*	Indian elm	leaf, root, stem	GC/MS	India	A. Kavitha *et al.*, 2014 [195]
n-Butyl ethyl phthalate (**100**)	*Stevia rebaudiana Bert*	Seasonal plant (Asteraceae)	leaf	GC/MS	Ishurdi, Pabna, Bangladesh	M.A. Hossain *et al.*, 2010 [196]
n-Butyl n-hexyl phthalate (**101**)	*Curvularia senegalensis*	Filamentous fungus (isolated from soil)	culture medium	GC/MS	Brazil	E.M.F. Lucas *et al.*, 2008 [108]
n-Butyl-isobutyl phthalate (**95**)	*Lentzea violacea AS 08*	Actinobacterium (isolated from soil of Himalayan ecosystem)		IR, MS, ^{1}H NMR, ^{13}C NMR, HSQC NMR	Himalaya, India	A. Hussain *et al.*, 2017 [197]
n-Butyl-isobutyl phthalate (**95**)	*Laminaria japonica*	kelp		^{1}H NMR, ^{13}C NMR, MS	Rongcheng, China	T. Bu *et al.*, 2010 [149]
n-Butyl-isobutyl phthalate (**95**)	*Melodinus fusiformis*	Plant (*Apocynaceae*)	leaf, twig	GC/MS	China	D. Wang *et al*, 2012 [198]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
n-Butyl-isobutyl phthalate (**95**)	*Dalbergia cochinchinensis*	Thailand rosewood (Fabaceae)		^{1}H NMR, ^{13}C NMR	Fangchenggang, Guangxi, China	R. Liu *et al.*, 2015 [199]
n-Butyl-isobutyl phthalate (**95**)	*Lythrum salicaria*	Flowering plant	whole plant	GC/MS	Sapporo, Japan	E. Fujita *et al.*, 1972 [200]
n-Butyl-isobutyl phthalate (**95**)	*Trichoderma harzianum*	fungus		GC/MS	Nani, Allahabad, and Pipri, Faizabad, India	A. Mishra *et al.*, 2018 [194]
n-Butyl-2-(8-methylnonyl) phthalate (**106**)	*Trichoderma asperellum*	filamentous fungus	culture filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
n-Butyl nonyl phthalate (**103**)	*Trichoderma harzianum*	fungus		GC/MS	Nani, Allahabad, and Pipri, Faizabad, India	A. Mishra *et al.*, 2018 [194]
n-Butyl octyl phthalate (**102**)	*Alnus nitida*	West Himalayan alder	stem bark	GC/MS	Swat, Pakistan	M. Sajid *et al.*, 2017 [201]
n-Butyl octyl phthalate (**102**)	*Trichoderma asperellum*	filamentous fungus	culture filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
n-Butyl octyl phthalate (**102**)	*Canthium parviflorum Lam. (Plectoria parviflora)*	(Rubiaceae)	callus, leaf	GC/MS	Andhra Pradesh, India	S.C. Kala *et al.*, 2017 [202]
n-Butyl octyl phthalate (**102**)	*Amaranthus caudatus L.*	annual flowering plant		GC/MS	China	L.Y. Qin *et al.*, 2015 [98]
n-Butyl octyl phthalate (**102**)	*Launaea arboresens*	Flowering plant (Asteraceae)	essential oil	GC/MS	Algerian Sahara	A. Cheriti *et al.*, 2006 [154]
n-Butyl undecyl phthalate (**105**)	*Brassica juncea L.*	mustard plant	leaf	GC/MS	Punjab, India	A. Sharma *et al.*, 2017 [203]
n-Butyl undecyl phthalate (**105**)	*Cenchrus ciliaris*	Dhaman grass	whole plant	GC/MS	Jodhpur, Rajasthan, India	P. Singariya *et al.*, 2015 [204]
Didecyl phthalate (**108**)	*Caulerpa racemosa* (O. Dargent)	green algae	volatile constituents	GC/MS	Egypt	N.E. Awad, 2002 [168]
Didecyl phthalate (**108**)	*Codium tomentosum* (Stackhouse)	green algae	volatile constituents	GC/MS	Egypt	N.E. Awad, 2002 [168]
Didodecyl phthalate (**110**)	*Brassica juncea L.*	mustard plant	leaf	GC/MS	Punjab, India	A. Sharma *et al.*, 2017 [203]
Diethyl phthalate (**7**)	*Helicobacter pylori*	gram negative bacterium	culture filtrate	GC/MS, HPLC	Californian laboratory, USA	Keire *et al.*, 2001 [205]
Diethyl phthalate (**7**)	*Canthium parviflorum Lam. (Plectoria parviflora)*	(Rubiaceae)	callus, leaf	GC/MS	Andhra Pradesh, India	S.C. Kala *et al.*, 2017 [202]
Diethyl phthalate (**7**)	*Moringa oleifera*	Drumstick tree (Moringaceae)	root	GC/MS	HEJICCBS garden, University of Karachi, Pakistan	S. Faizi *et al.*, 2014 [206]
Diethyl phthalate (**7**)	*Moringa oleifera*	Drumstick tree (Moringaceae)	leaf		Thanjavur, Tamil Nadu, India	S. Karthika *et al.*, 2013 [172]
Diethyl phthalate (**7**)	*Tecoma radicans (Campsis radicans)*	Bignoniaceae	leaf	GC/MS	Egypt	F.A. Hashem *et al.*, 2006 [207]
Diethyl phthalate (**7**)	*Artocarpus lakoocha Roxb.*		leaf	GC/MS	Kolkata, India	E. Bhattacharya, *et al.*, 2019 [208]
Diethyl phthalate (**7**)	*Penicillium olsonii*	filamentous fungus	Cultural filtrate	IR, EI-MS, ^{1}H NMR, ^{13}C NMR	Laboratory, France	P. Amade *et al.*, 1994 [209]
Dimethyl phthalate (**7**)	*Amaranthus caudatus L.*	annual flowering plant		GC/MS	China	L.Y. Qin *et al.*, 2015 [98]
Dimethyl phthalate (**7**)	*Eucryphia cordifolia Cav.*	Chilean Ulmo (Cunoniaceae)	honey	GC/MS	Puerto Varas, Chile	E. Acevedo *et al.*, 2017 [210]
Dimethyl phthalate (**7**)	*Syzygium cumini*	Malabar plum (Myrtaceae)	bark	GC/MS	Madhya Pradesh, India	Mehta, B.K. *et al.*, 2012 [211]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Dimethyl phthalate (**7**)	*Cryptotaenia canadensis DC.*	Canadian honewort (perennial plant)			Japan	S. Hayashi *et al.*, 1967* [158]
Di-n-amyl phthalate (**19**)	*Cryptotaenia canadensis DC.*				Japan	S. Hayashi *et al.*, 1967* [158]
Di-n-butyl phthalate (**5**)	*Cryptotaenia canadensis DC.*				Japan	S. Hayashi *et al.*, 1967* [158]
Di-n-butyl phthalate (**5**)	*Calliandra haematocephala Hassk.*	Flowering plant (Fabaceae)	aerial parts	GC/MS	Egypt	A.H.S. Abou Zeid *et al.*, 2006 [155]
Di-n-butyl phthalate (**5**)	*Cladophora fracta*	green algae		GC/MS	Different locations in Taiwan	B. Babu and J.-T. Wu, 2010 [212]
Di-n-butyl phthalate (**5**)	*Sargassum confusum*	brown macroalgae	whole algae	^{1}H NMR, ^{13}C NMR, MS	S.-Korea	V.S. Ganti *et al.*, 2006 [213]
Di-n-butyl phthalate (**5**)	*Streptomyces nasri*	gram positive bacterium		^{1}H NMR, ^{13}C NMR	Laboratory, Egypt	M.Y.M. El-Naggar, 1997 [214]
Di-n-butyl phthalate (**5**)	*Chlorella sp.*	single-celled green algae		GC/MS	Different locations in Taiwan	B. Babu and J.-T. Wu, 2010 [212]
Di-n-butyl phthalate (**5**)	*Launaea arboresens*	Flowering plant (Asteraceae)	essential oil	GC/MS	Algerian Sahara	A. Cheriti *et al.*, 2006 [154]
Di-n-butyl phthalate (**5**)	*Cinachyrella cavernosa (Lamarck)*	demosponge		GC/MS	Goa, India	S. Wahidullah *et al.*, 2015 [72]
Di-n-butyl phthalate (**5**)	*Bangia atropurpurea*	red algae			Taiwan	C.Y. Chen, 2004 [141]
Di-n-butyl phthalate (**5**)	*Hydrodictyon reticulatum*	water net green algae		GC/MS	Different locations in Taiwan	B. Babu and J.-T. Wu, 2010 [212]
Di-n-butyl phthalate (**5**)	*Microcystis aeruginosa*	freshwater cyanobacterium		GC/MS	Different locations in Taiwan	B. Babu and J.-T. Wu, 2010 [212]
DI-n-butyl phthalate (**5**)	*Phormidium sp.*	cyanobacterium		GC/MS	Different locations in Taiwan	B. Babu and J.-T. Wu, 2010 [212]
Di-n-butyl phthalate (**5**)	*Undaria pinnatifida*	edible seaweed (wakame, sea mustard)		^{14}C natural abundance measurements	Kanazawahakkei, Yokohama, Japan	M. Namikoshi *et al.*, 2006 [215]
Di-n-butyl phthalate (**5**)	*Laminaria japonica*	brown algae		^{14}C natural abundance measurements	Hachinohe, Aomori, Japan	M. Namikoshi *et al.*, 2006 [215]
Di-n-butyl phthalate (**5**)	*Stoechospermum marginatum (C. agardh) Kuetzing*	brown algae	whole algae		Goa, India	S. Wahidulla, 1995 [169]
Di-n-butyl phthalate (**5**)	*Ulva sp.*	edible green algae sea lettuce		^{14}C natural abundance measurements	Yokohama Marine Park, Yokohama, Japan	M. Namikoshi *et al.*, 2006 [215]
Di-n-butyl phthalate (**5**)	*Spirogyra sp.*	filamentous green algae (water silk)		GC/MS	Various locations in Taiwan	B. Babu and J.-T. Wu, 2010 [212]
Di-n-butyl phthalate (**5**)	*Caulerpa racemosa* (O. Dargent)	green algae	volatile constituents	GC/MS	Egypt	N.E. Awad, 2002 [168]
Di-n-butyl phthalate (**5**)	*Streptomyces melanosporofaciens*	gram-positive bacterium			S.-Korea	D.-S. Lee, 2000 [216]
Di-n-butyl phthalate (**5**)	*Streptomyces albidoflavus*	gram-positive bacterium			Laboratory, India	R. N. Roy *et al.*, 2006 [217]
Di-n-butyl phthalate (**5**)	*Trichoderma harzianum*	fungus		GC/MS	Nani, Allahabad, and Pipri, Faizabad, India	A. Mishra *et al.*, 2018 [194]
Di-n-butyl phthalate (**5**)	*Rhizosphere actinomycetes*	gram-positive, filamentous bacterium	Isolated from soil samples	GC/MS	Kota, Jaipur, Alwar, Udaipur in Rajasthan, India	N. Kumari *et al.*, 2020 [100]
Di-n-butyl phthalate (**5**)	*Endophytic fungus of Rumex madaio*	Endophytic fungus		^{1}H NMR, ^{13}C NMR	Putuo Island, Zhoushan, China	X. Bai *et al.*, 2019 [101]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Di-n-butyl phthalate (**5**)	*Flowers of Sophora japonica var. violacea*	Japanese pagoda tree		^{1}H NMR, ^{13}C NMR	Dalian, China	J. Yang *et al.*, 2018 [218]
Di-n-butyl phthalate (**5**)	*Salicornia herbacea*	halophyte flowering plant		^{1}H NMR, MS	Yancheng City, Jiangsu, China	X. M. Wang *et al.*, 2013 [219]
Di-n-butyl phthalate (**5**)	*Melodinus fusiformis*	Plant (Apocynaceae)	leaf, twig	GC/MS	China	D. Wang *et al.*, 2012 [198]
Di-n-butyl phthalate (**5**)	*Nocardia levis MK-Vl_113*	actinobacterium		MS of a mixture	Guntur, India	A. Kavitha *et al.*, 2010 [220] A. Kavitha *et al.*, 2009 [97]
Di-n-butyl phthalate (**5**)	*Streptomyces sp. strain 6803*	gram-positive bacterium			China	M. Chen *et al.*, 2009 [221]
Di-n-butyl phthalate (**5**)	*Trichoderma asperellum*	filamentous fungus			China	C. Tian *et al.*, 2016 [142]
Di-n-butyl phthalate (**5**)	*Aspergillus niger*	filamentous fungus			China	C. Tian *et al.*, 2016 [142]
Di-n-butyl phthalate (**5**)	*Ipomoea carnea*	flowering plant (pink morning glory)		^{1}H NMR and ^{13}C NMR	Puna, India	E. Khatiwora *et al.*, 2011 [222] V.B. Adsul *et al.*, 2012 [223]
Di-n-butyl phthalate (**5**)	*Callianthemum taipaicum*	rhizomatous herb		MS, ^{1}H NMR, ^{13}C NMR	Taibai Mt., Shaanxi, China	D.M. Wang *et al.*, 2012 [224]
Di-n-butyl-phthalate (**5**)	*Zygomycale sp.*	marine sponge		GC-MS		J.A. Johnson *et al.*, 2012 [225]
Di-n-butyl phthalate (**5**)	*(marine) Pseudomonas sp.* PB01	gram negative bacterium		^{1}H NMR, ^{13}C NMR, COSY, DEPT, HMBC NMR	GenBank Accession No. EU126129	V.L.T. Hoang *et al.*, 2008 [179]
Di-n-butyl phthalate (**5**)	*Paraconiothyrium variabile* (fungus) on *Aquilaria sinensis* (plant)	fungus producing agilawood		GC/MS	China	J.L. Cui *et al.*, 2013 [226]
Di-n-butyl phthalate (**5**)	*Sisymbrium officinale*	hedge mustard (plant)			Split, Croatia	I. Blažević *et al.*, 2010 [227]
Di-n-butyl phthalate (**5**)	*Brevibacterium McBrellneri*	gram positive actinobacterium		IR, ^{1}H NMR, ^{13}C NMR	MTCC, IMTECH, Chandigarh, India (procurement)	M. Rajamanik-yam *et al.*, 2017 [164]
Di-n-butyl phthalate (**5**)	*Rheinheimera japonica KMM 9513*^{T}	marine bacterium			Sea of Japan	N.I. Kalinovskaya *et al.*, 2017 [165]
Di-n-butyl phthalate (**5**)	*Exserohilum monoceras*	fungus		GC/MS	China	Y. Chen *et al.*, 2009 [228]
Di-n-butyl phthalate (**5**)	*Pseudomonas stutzeri*	gram negative bacterium			China	X.J. Gu *et al.*, 2011 [229]
Di-n-butyl phthalate (**5**)	*Aspergillus parasiticus* grown on hazelnuts	fungus		HPLC-MS		P. Basaran *et al.*, 2010 (authors qualify that the phthalate can be of anthropo-genic origin) [230]
Di-n-butyl phthalate (**5**)	*Uncaria rhynchophylla*	Plant (Cat's claw herb)		NMR, MS	China (market purchased material)	Y.-L. Wang *et al.*, 2018 [231]
Di-n-butyl phthalate (**5**)	*Leucas zeylanica*	Ceylon slitwort (Lamiaceae)		NMR, incl. 2D-NMR, MS	Haikou, China	N. Nidhal *et al.*, 2020 [232]
Di-n-butyl phthalate (**5**)	*Dolomiaea souliei*	Flowering plant (Asteraceae)			China	H. Wei *et al.*, 2012 [233]
Di-n-butyl phthalate (**5**)	*Durian fruit (peel)*	tree	volatile constituents of fruit peel	GC/MS	China	B. Zhang *et al.*, 2012 [192]
Di-n-butyl phthalate (**5**)	*Lantana camara L.*	Perennial shrub	essential oil	GC/MS	China	L. Ren *et al.*, 2016 [184]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Di-n-butyl phthalate (**5**)	*Sarcophyton glaucum*	Rough leather coral		^{1}H NMR, ^{13}C NMR, 2D-NMR	Sanya Bay, Hainan Island, China	C.X. Zhang *et al.*, 2013 [189]
Di-n-butyl phthalate (**5**)	*Lythrum salicaria*	Flowering plant	whole plant	GC/MS	Sapporo, Japan	E. Fujita *et al.*, 1972 [200]
Di-n-butyl phthalate (**5**)	*Verbena venosa, V. hybrida, V. supina, V. bonariensis*	Flowering plant	volatile components of aerial parts	GC/MS	Nasar City, Cairo, Egypt	H. Al-Amier *et al.*, 2005 [234]
Di-n-butyl phthalate (**5**)	*Trichoderma asperellum*	filamentous fungus	culture filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
Di-n-butyl phthalate (**5**)	*Coleus foskohlii* (*Plectranthus barbatus)*	Perennial plant	essential oil	GC/MS	India	S. Takshak *et al.*, 2016 [235]
Di-n-butyl phthalate (**5**)	*Rhizophora apiculata*	Mangrove plant	leaf	GC/MS	Tamil Nadu, India	C.C.J. Paranjothi *et al.*, 2018 [236]
Di-n-butyl phthalate (**5**)	*Lysimachia microcarpa*	(Primulaceae)	essential oil	GC/MS	China	Z. Ding *et al.*, 1993 [237]
Di-n-butyl phthalate (**5**)	*Capsicum chinense*	Chili pepper (Solanaceae)	Root exudate	GC/MS	China	X. Han, *et al.*, 2015 [238]
Di-n-butyl phthalate (**5**)	*Cupressus sempervirens*	Mediterranean cypress (Cupressaceae)	bark and leaf	GC/MS	Al-Jabel Al-Akhdar Region, Libya	M.E.I. Badawy *et al.*, 2019 [239]
Di-n-butyl phthalate (**5**)	*Tecoma radicans (Campsis radicans)*	Bignoniaceae	leaf	GC/MS	Egypt	F.A. Hashem *et al.*, 2006 [207]
Di-n-butyl phthalate (**5**)	*Morus alba*	White mulberry	leaf	GC/MS	Aceh, Indonesia	R. Nasution *et al.*, 2015 [240]
Di-n-butyl phthalate (**5**)	*Morus alba*	White mulberry	leaf	GC/MS	China	Y. Yang *et al.*, 2011 [241]
Di-n-butyl phthalate (**5**)	*Brosimum glaziovii*	Moraceae	Leaf and branch	GC/MS	Botanical Garden, Sao Paulo, Brazil	A. Coqueiro *et al.*, 2014 [242]
Di-n-butyl phthalate (**5**)	*Artocarpus nanchuanensis*	Moraceae	Fruiting branch	^{1}H and ^{13}C NMR	Nanchuan District, Chongqing City, China	G. Ren *et al.*, 2013 [243]
Di-n-butyl phthalate (**5**)	*Ficus benghalensis* L.	Moraceae	Stem bark	GC/MS	Egypt	F. Darwish, 2002 [244]
Dicyclohexyl phthalate (**11**)	*Sargassum confusum*	brown macroalgae	whole algae	^{1}H NMR, ^{13}C NMR	S.-Korea	V.S. Ganti *et al.*, 2006 [213]
Dicyclohexyl phthalate (**11**)	*Tecoma radicans (Campsis radicans)*	Bignoniaceae	leaf	GC/MS	Egypt	F.A. Hashem *et al.*, 2006 [207]
Diethyl phthalate (**7**)	*Avicennia officinalis*	Indian mangrove		GC/MS	Tamil Nadu, India	V.B. Bhimba *et al.*, 2013 [245]
Diethyl phthalate (**7**)	*Streptomyces cheonanensis VUK-A*	gram-positive bacterium (isolated from mangrove ecosystem)			Coringa, Gulf of Bengal, Andhra Pradesh	U. Mangamuri *et al.*, 2016 [246]
Diethyl phthalate (**7**)	*Vicia villosa* Roth	Hairy vetch (legume)			Gyeongsan, S.-Korea	M.T. Islam *et al.*, 2013 [181]
Diethyl phthalate (**7**)	*Syzygium cumini*	Malabar plum (Myrtaceae)	bark	GC/MS	Madhya Pradesh, India	Mehta, B.K. *et al.*, 2012 [211]
Diethyl phthalate (**7**)	*Undaria pinnatifida*	edible seaweed (wakame, sea mustard)		^{14}C natural abundance measurements	Kanazawahakkei, Yokohama, Japan	M. Namikoshi *et al.*, 2006 [215]
Diethyl phthalate (**7**)	*Laminaria japonica*	brown algae		^{14}C natural abundance measurements	Hachinohe, Aomori, Japan	M. Namikoshi *et al.*, 2006 [215]
Diethyl phthalate (**7**)	*Ulva sp.*	edible green algae sea lettuce		^{14}C natural abundance measurements	Yokohama Marine Park, Yokohama, Japan	M. Namikoshi *et al.*, 2006 [215]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
2, 12-Diethyl-11-methylhexadecyl 2-ethyl-11-methylhexadecyl phthalate (**96**)	*Hippocampus kuda Bleeler*	seahorse	Whole body	HRMS, MS, IR, UV, ^{1}H NMR, ^{13}C NMR	Zhoushan Island, Zhejiang, China	Z.J. Qian *et al.*, 2012 [173] Y. Li *et al.*, 2008 [152]
Di-n-heptyl phthalate (**111**)	*Trichoderma asperellum*	filamentous fungus	culture filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
Di-n-hexyl phthalate (**14**)	*Cryptotaenia canadensis DC.*	Canadian honewort (perennial plant)			Japan	S. Hayashi *et al.*, 1967* [158]
Di-n-hexyl phthalate (**14**)	*Ligusticum porteri*	Apiaceae	callus, aerial part, root	GC/MS	Chihuahua, Mexico,	D. Goldhaber-Pasillas *et al.*, 2012 [170]
Di-n-hexyl phthalate (**14**)	*Verbena venosa, V. hybrida, V. supina, V. bonariensis*	Flowering plant	volatile components of aerial parts	GC/MS	Nasar City, Cairo, Egypt	H. Al-Amier *et al.*, 2005 [234]
Di-n-hexyl phthalate (**14**)	*Flue cured tobacco (Nicotiana)*		Rhizosphere soils of		Mengtong of Shandong province, China	X. Ren *et al.*, 2015 [145]
Di-n-hexyl phthalate (**14**)	*Trichoderma asperellum*	filamentous fungus	culture filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
Di-n-hexyl phthalate (**14**)	*Ficus carica L*	Common fig	volatile oil	GC/MS	China	J. Tian *et al.*, 2005 [247]
Diisobutyl phthalate (**12**)	*Telfairia occidentalis Hook*	Fluted pumpkin (Cucurbitaceae)	seed	GC/MS	Uyo, Nigeria	O.A. Eseyin *et al.*, 2018 [248]
Diisobutyl phthalate (**12**)	*Amaranthus caudatus L.*	annual flowering plant		GC/MS	China	L.Y. Qin *et al.*, 2015 [98]
Isobutyl 2-pentyl phthalate (**112**)	*Trichoderma harzianum*	fungus		GC/MS	Nani, Allahabad, and Pipri, Faizabad, India	A. Mishra *et al.*, 2018 [194]
Di-isooctyl phthalate (**16**)***	*Sclerotium cepivorum*	Fungus (Ascomycota)		GC/MS	Dakahlia and Gharbia, Egypt	E.A. Elsherbiny *et al.*, 2015 [249]
Di-isooctyl phthalate (**16**)	*Telfairia occidentalis Hook*	Fluted pumpkin (Cucurbitaceae)	seed	GC/MS	Uyo, Nigeria	O.A. Eseyin *et al.*, 2018 [248]
Di-isooctyl phthalate[x]	*Amaranthus caudatus L.*	annual flowering plant		GC/MS	China	L.Y. Qin *et al.*, 2015 [98]
Di-isooctyl phthalate (**16**)	*Ficus carica L*	Common fig	volatile oil	GC/MS	China	J. Tian *et al.*, 2005 [247]
*Di-isononyl phthalate (DINP-2)*** ** (**15**)	*Pterocarpus erinaceus*	tree	stem bark	GC/MS	Nsukka, Enugu State, Nigeria	A.F. Gabriel *et al.*, 2009 [250]
Di-isononyl phthalate (**15**)	*Sclerotium cepivorum*	Fungus (Ascomycota)		GC/MS	Dakahlia and Gharbia, Egypt	E.A. Elsherbiny *et al.*, 2015 [249]
Di-isononyl phthalate (**15**)	*Calliandra haematocephala Hassk.*	Flowering plant (Fabaceae)	aerial parts	GC/MS	Egypt	A.H.S. Abou Zeid *et al.*, 2006 [155]
Di-isononyl phthalate (**15**)	*Caulerpa racemosa* (O. Dargent)	green algae	volatile constituents	GC/MS	Egypt	N.E. Awad, 2002 [168]
Di-isononyl phthalate (**15**)	*Codium tomentosum* (Stackhouse)	green algae	volatile constituents	GC/MS	Egypt	N.E. Awad, 2002 [168]
Di-isononyl phthalate (**15**)	*Sargassum confusum*	brown macroalgae	whole algae	^{1}H NMR, ^{13}C NMR	S.-Korea	V.S. Ganti *et al.*, 2006 [213]
Di-isononyl phthalate (**15**)	*Astragalus membranaceus*	Flowering plant (Fabaceae)	root		S.-Korea	J.S. Kim *et al.*, 1996 [251]
Di-isononyl phthalate (**15**)	*Stoechospermum marginatum (C. agardh) Kuetzing*	brown algae	whole algae		Goa, India	S. Wahidulla, 1995 [169]
Di-n-pentyl phthalate (**19**)	*Trichoderma asperellum*	filamentous fungus	culture filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
Di-n-pentyl phthalate (**19**)	*Sindora glabra*	tree (Fabaceae)	leaf		China	J.F. Zhang *et al.*, 2016 [252]
Di-n-pentyl phthalate (**19**)	*Chaenomeles sinensis (Pseudocydonia sinensis)*	Chinese quince (deciduous tree)	fruit		China	H.Y. Liang *et al.*, 2013 [253]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Di-n-pentyl phthalate (**19**)*******	*Codonopsis pilosula*	perennial flowering plant		^{1}H NMR, ^{13}C NMR, MS	Tanchang country, Gansu Province, China	N. Xie *et al.*, 2017 [254]
Ditridecyl phthalate (**40**)	*Rhododendron arboreum* Sm	tree rhododendron (Ericaceae)	flower	GC/MS	Punjab, India	V. Gautam *et al.*, 2016 [255]
Ditridecyl phthalate (**40**)	*Ficus carica L*	Common fig	volatile oil	GC/MS	China	J. Tian *et al.*, 2005 [247]
Ethyl phthalate (**62**)	*Patrinia villosa* Juss	(Caprifoliaceae)	essential oil	GC/MS	China	X.P. Liu *et al.*, 2008 [256]
Ethyl methyl phthalate (**23**)	*Carduus pycnocephalus L.*	Italian thistle	essential oil	GC/MS	Al-Hada, Saudi Arabia	L.A. Al-Shammari *et al.*, 2012 [111]
Ethyl methyl phthalate (**23**)	*Datura stramonium L.*	Thorn apple	stem	GC/MS, FT-IR	Turkey	H. Durak and T. Aysu, 2016 [110]
Ethyl methyl phthalate (**23**)	*Isatis indigotica*	Dyer's woad	liposoluble constituents	GC/MS	China	J. Wu *et al.*, 2008 [112]
Ethyl methyl phthalate (**23**)	*Salvia sclarea L.*	Clary sage	volatile oils	GC/MS, GC/FTIR	China	J. Cai *et al.*, 2006 [257]
n-Heptyl n-propyl phthalate (**114**)	*Curvularia senegalensis*	Filamentous fungus (isolated from soil)	culture medium	GC/MS	Brazil	E.M.F. Lucas *et al.*, 2008 [108]
n-Hexyl phthalate (**27**)	*Hirsutella citriformis*	fungus		GC/MS	India	A. Ramachan-dran *et al.*, 2013 [258]
n-Hexyl n-propyl phthalate (**113**)	*Curvularia senegalensis*	Filamentous fungus (isolated from soil)	culture medium	GC/MS	Brazil	E.M.F. Lucas *et al.*, 2008 [108]
2-(4-Hydroxybutyl)butyl methyl phthalate (**116**)	*Alnus nitida*	West Himalayan alder	stem bark	GC/MS	Swat, Pakistan	M. Sajid *et al.*, 2017 [201]
Cyclohexyl phthalate (**117**)	*Polygonum aviculare*	Common knotgrass	Essential oil	GC/MS	China	F.Q. Xu *et al.*, 2012 [259]
Decyl butyl phthalate (2 undefined isomers) (**104**)	*Curvularia senegalensis*	Filamentous fungus (isolated from soil)	culture medium	GC/MS	Brazil	E.M.F. Lucas *et al.*, 2008 [108]
Decyl butyl phthalate (**104**)	*Telfairia occidentalis*	Fluted pumpkin (Cucurbitaceae)	seed	GC/MS	Uyo, Nigeria	O.A. Eseyin *et al.*, 2018 [248]
Di-isoamyl phthalate (**118**)	*Cryptotaenia canadensis DC.*	Canadian honewort (perennial plant)			Japan	S. Hayashi *et al.*, 1967* [158]
Di-isobutyl phthalate (**12**)	*Cryptotaenia canadensis DC.*	Canadian honewort (perennial plant)			Japan	S. Hayashi *et al.*, 1967* [158]
Di-isobutyl phthalate (**12**)	*Streptomyces sp. strain 6803*	gram-positive bacterium			China	M. Chen *et al.*, 2009 [221]
Di-isobutyl phthalate (**12**)	*Rheinheimera japonica KMM 9513^T*	marine bacterium			Sea of Japan	N.I. Kalinovskaya *et al.*, 2017 [165]
Di-isobutyl phthalate (**12**)	*Aquilariae resinatum*	(Thymelaeaceae)	volatile components	GC/MS	Hainan, China	N. Lin *et al.*, 2016 [260]
Di-isobutyl phthalate (**12**)	*Scaligeria nodosa*	flowering plant (Apiaceae)	essential oil	GC/MS	Bamu Mt., Shiraz, Iran	A.R. Jassbi *et al.*, 2017 [261]
Di-isobutyl phthalate (**12**)	*Lantana camara L.*	Perennial shrub	essential oil	GC/MS	China	L. Ren *et al.*, 2016 [184]
Di-isobutyl phthalate (**12**)	*Lythrum salicaria*	Flowering plant	whole plant	GC/MS	Sapporo, Japan	E. Fujita *et al.*, 1972 [200]
Di-isobutyl phthalate (**12**)	*Trichoderma asperellum*	filamentous fungus	culture filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
Di-isobutyl phthalate (**12**)	*Rhizophora apiculata*	Mangrove plant	leaf	GC/MS	Tamil Nadu, India	C.C.J. Paranjothi *et al.*, 2018 [236]
Di-isobutyl phthalate (**12**)	*Holoptelea integrifolia*	Indian elm	root, stem, leaf	GC/MS	India	A. Kavitha *et al.*, 2014 [195]
Di-isobutyl phthalate (**12**)	*Astilbe chinensis*	(Saxifragaceae)	volatile oil	GC/MS	China	T. Yang *et al.*, 2011 [96]
Di-isobutyl phthalate (**12**)	*Capsicum chinense*	Chili pepper (Solanaceae)	Root exudate	GC/MS	China	X. Han *et al.*, 2015 [238]
Di-isopropyl phthalate (**42**)	*Cinachyrella cavernosa*	demosponge		GC/MS	Goa, India	S. Wahidullah *et al.*, 2015 [72]
Di-n-octyl phthalate (**20**)	*Sargassum confusum*	brown macroalgae	whole algae	^{1}H NMR, ^{13}C NMR, MS	S.-Korea	V.S. Ganti *et al.*, 2006 [213]
Di-n-octyl phthalate (**20**)	*Sargassum wightii*	brown macroalgae			India	V.M.V.S. Sastry *et al.*, 1995 [262]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Di-n-octyl phthalate (**20**)	*Salicornia herbacea*	halophyte flowering plant		^{1}H NMR, MS	Yancheng City, Jiangsu, China	X. M. Wang *et al.*, 2013 [219]
Di-n-octyl phthalate (**20**)	*Launaea arboresens*	Flowering plant (Asteraceae)	essential oil	GC/MS	Algerian Sahara	A. Cheriti *et al.*, 2006 [154]
Di-n-octyl phthalate (**20**)	*Streptomyces parvus*	gram-positive bacterium (from seawater and sediment samples)		GC/MS	Suez Bay, Egypt	H. Abd-Elnaby *et al.*, 2016 [263]
Di-n-octyl phthalate (**20**)	*Nigella glandulifera* Freyn.	annual plant (Ranunculaceae)				D.T.M. Nguyen *et al.*, 2007 [151]
Di-n-octyl phthalate (**20**)	*Lonicera quinquelocularis*	translucent honeysuckle		^{1}H NMR, ^{13}C NMR	Pakistan	D. Khan *et al.*, 2014 [133.134]
Di-n-octyl phthalate (**20**)	*Lythrum salicaria*	Flowering plant	whole plant	GC/MS	Sapporo, Japan	E. Fujita *et al.*, 1972 [200]
Di-n-octyl phthalate (**20**)	*Trichoderma asperellum*	filamentous fungus	culture filtrate	GC/MS	Pantnagar, India	N.R. Bhardwaj *et al.*, 2017 [190]
Diisooctyl phthalate (**16**)	*Fomitiporia punctata*	Fungus (Hymenochaetaceae)	ethanolic extract	GC/MS	China	F. Zhu *et al.*, 2011 [193]
Diisooctyl phthalate (**16**)	*Trichoderma harzianum*	fungus		GC/MS	Nani, Allahabad, and Pipri, Faizabad, India	A. Mishra *et al.*, 2018 [194]
Di-n-octyl phthalate (**20**)	*Hibiscus micranthus*	Malvaceae	root	GC/Ms	Telangana, India	K.A. Kumar *et al.*, 2011 [153]
Di-n-octyl phthalate (**20**)	*Cenchrus ciliaris*	Dhaman grass	whole plant	GC/MS	Jodhpur, Rajasthan, India	P. Singariya *et al.*, 2015 [204]
Di-n-octyl phthalate (**20**)*****	*Euphorbia thymifolia*	annual plant	whole plant	GC/MS	Madhya Pradesh, India	R. Shrivastava *et al.*, 2019 [264]
Di-n-octyl phthalate (**20**)	*Pachygone ovata*	climbing shrub			India	L.E. Amalarasi *et al.*, 2019 [150]
Di-n-octyl phthalate (**20**)	*Saccharomyces cerevisiae*	baker's yeast		GC/MS		M.M. Abdel-Kareem *et al.*, 2019 [265]
Di-n-octyl phthalate (**20**)	*Plumbago zeylanica, Linn.*	herbaceous plant	leaf	GC/MS	Jaipur, India	I. Sharma *et al.*, 2015 [266]
Di-n-octyl phthalate (**20**)	*Memnoniella*	fungus	culture medium	GC/MS	Melghat forest, Amravat, India	H. Dilip *et al.*, 2015 [267]
Di-n-octyl phthalate (**20**)	*Coleus foskohlii (Plectranthus barbatus)*	Perennial plant	essential oil	GC/MS	India	S. Takshak *et al.*, 2016 [235]
Di-n-octyl phthalate (**20**)	*Aloe vera*	succulent plant	leaf	GC/MS	Tamil Nadu, India	T. Jeevitha *et al.*, 2018 [88]
Di-n-octyl phthalate (**20**)	*Vernonia amygdalina*	(Asteraceae)	leaf	GC/MS	Zaria, Nigeria	S.S. Bello *et al.*, 2018 [268]
Di-n-octyl phthalate (**20**)	*Alstonia boonei*	Deciduous tropical-forest tree	stem bark	GC/MS	Okpuje, Enugu State, Nigeria	A.A. Imam *et al.*, 2017 [175]
Di-n-octyl phthalate (**20**)	*Canthium parviflorum Lam. (Plectoria parviflora)*	(Rubiaceae)	callus, leaf	GC/MS	Andhra Pradesh, India	S.C. Kala *et al.*, 2017 [202]
Di-n-octyl phthalate (**20**)	*Astilbe chinensis*	(Saxifragaceae)	volatile oil	GC/MS	China	T. Yang *et al.*, 2011 [96]
Di-octyl phthalate (**20**)******	*Suaeda glauca*	Seepweeds, halophilic plants	stem, leaf, root	GC/MS	Hulunbuir, China	X. Lu *et al.*, 2019 [269]
Di-octyl phthalate (**20**)******	*Puccinellia tenuiflora*	Alkali grass (Poaceae)	stem, leaf, root	GC/MS	Hulunbuir, China	X. Lu *et al.*, 2019 [269]
Di-octyl phthalate (**20**)******	*Cyanthillium cinereum*	Perennial plant	essential oil	GC/MS	Tamil Nadu India	J. Dharani *et al.*, 2018 [270]
Di-octyl phthalate (**20**)******	*Rhizophora apiculata*	Mangrove plant	leaf	GC/MS	Tamil Nadu India	C.C.J. Paranjothi *et al.*, 2018 [236]
Di-octyl phthalate (**20**)******	*Brassica juncea L.*	Mustard plant	leaf	GC/MS	Punjab, India	A. Sharma *et al.*, 2017 [203]
Di-n-propyl phthalate (**22**)	*Holoptelea integrifolia*	Indian elm	leaf, stem, root	GC/MS	India	A. Kavitha *et al.*, 2014 [195]
Di-n-propyl phthalate (**22**)	*Astilbe chinensis*	(Saxifragaceae)	volatile oil	GC/MS	China	T. Yang *et al.*, 2011 [96]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
Di-n-propyl phthalate (**22**)	*Lysimachia microcarpa*	(Primulaceae)	essential oil	GC/MS	China	Z. Ding *et al.*, 1993 [237]
Di-n-propyl phthalate (**22**)	*Lysimachia nummularia aurea*	(Primulaceae)	essential oil	GC/MS	China	J.F. Wei *et al.*, 2013 [271]
Diundecyl phthalate (**109**)	*Hygrophila auriculata*	Medicinal plant (Acanthaceae)		GC/MS	Tiruchirapalli District, Tamil Nadu, India	A.Z. Hussain *et al.*, 2013 [272]
Diundecyl phthalate (**109**)	*Magnolia officinalis*	(Magnoliaceae)	volatile oil	GC/MS	China	Y. Lu *et al.*, 2011 [273]
Isodecyl octyl phthalate (**119**)	*Trichoderma harzianum*	fungus		GC/MS	Nani, Allahabad, and Pipri, Faizabad, India	A. Mishra *et al.*, 2018 [194]
2-Ethyldecyl 2-ethylundecyl phthalate (**97**)	*Hippocampus kuda Bleeler*	seahorse	whole body	HRMS, MS, IR, ^{1}H NMR, ^{13}C NMR	Zhoushan Island, Zhejiang, China	Z.J. Qian *et al.*, 2012 [173] Y. Li *et al.*, 2008 [152]
Ethyl heptyl phthalate (**120**)	*Curvularia senegalensis*	Filamentous fungus (isolated from soil)	culture medium	GC/MS	Brazil	E.M.F. Lucas *et al.*, 2008 [108]
Ethyl 2-methylbutyl phthalate (**121**)	*Streptomyces cheonanensis VUK-A*	gram-positive bacterium (isolated from mangrove ecosystem)		^{1}H NMR, ^{13}C NMR, FT-IR, EI-MS	Coringa, Gulf of Bengal, Andhra Pradesh	U. Mangamuri *et al.*, 2016 [246]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Anabaena flos-aquae*	filamentous cyanobacterium		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Botryococcus braunii*	green algae		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Chlorella sp.*	single-celled green algae		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Cladophora fracta*	filamentous green algae		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Cylindrospermopsis raciborskii*	filamentous cyanobacterium		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Microcystis aeruginosa*	freshwater cyanobacterium		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Oscillatoria*	filamentous cyanobacterium		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Peridinium sp.*	marine dinoflagellate		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Peridinium bipes*	marine dinoflagellate		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Phormidium*	marine cyanobacterium		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Spirogyra sp.*	filamentous green algae (water silk)		GC/MS	Different lo-calities, Taiwan	B. Babu and J.-T. Wu, 2010 [212]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Trichoderma harzianum*	fungus		GC/MS	Nani, Allahabad, and Pipri, Faizabad, India	A. Mishra *et al.*, 2018 [194]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Ligusticum porteri*	Apiaceae	callus, aerial part, root	GC/MS	Chihuahua, Mexico,	D. Goldhaber-Pasillas *et al.*, 2012 [170]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Telfairia occidentalis Hook*	Fluted pumpkin (Cucurbitaceae)	seed	GC/MS	Uyo, Nigeria	Eseyin *et al.*, 2018 [248]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Capsicum chinense*	Chili pepper (Solanaceae)	Root exudate	GC/MS	China	X. Han, *et al.*, 2015 [238]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Cupressus sempervirens*	Mediterranean cypress (Cupressaceae)	bark and leaf	GC/MS	Al-Jabel Al-Akhdar Region, Libya	M.E.I. Badawy *et al.*, 2019 [239]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Juniperus phoenicea*	Phoenicean juniper (Cupressaceae)	Bark and leaf	GC/MS	Al-Jabel Al-Akhdar Region, Libya	M.E.I. Badawy *et al.*, 2019 [239]
2-Ethylhexyl phthalate (MEHP, **26***)*	*Sargassum wightii*	macro-algae		IR, ^{1}H NMR, ^{13}C NMR	Tuticorn, Tamil Nadu, India	D. Rosaline *et al.*, 2016 [274]
Isobutyl n-butyl phthalate (**95**)	*Cryptotaenia canadensis DC.*	Canadian honewort (perennial plant)			Japan	S. Hayashi *et al.*, 1967* [158]

Phthalate	Organism source	Description of organism	Extracted part of the organism	Identification method of the phthalate	Region/Location	Reference
n-Nonyl n-propyl phthalate (**115**)	*Curvularia senegalensis*	Filamentous fungus (isolated from soil)	culture medium	GC/MS	Brazil	E.M.F. Lucas *et al.*, 2008 [108]
Diheptyl phthalate (**111**)	*Aloe vera*	Succulent plant	gel	GC/MS	Tochigi, Japan	I. Yamaguchi *et al.*, 1993 [275]
*Diheptyl phthalate*** (**111**)	*Lythrum salicaria*	Flowering plant	whole plant	GC/MS	Sapporo, Japan	E. Fujita *et al.*, 1972 [200]
*Dinonyl phthalate*** (**107**)	*Lythrum salicaria*	Flowering plant	whole plant	GC/MS	Sapporo, Japan	E. Fujita *et al.*, 1972 [200]
n-Octyl phthalate (**28**)	*Chorisia chodatii*	Floss silk tree (Malvaceae)	flower	UV-VIS, ^{1}H NMR, ^{13}C NMR; MS	Minia University campus, Minia, Egypt	J. Refaat *et al.*, 2015 [276]
n-Octyl phthalate (**28**)	*Aloe vera*	Succulent plant	gel	GC/MS	Tochigi, Japan	I. Yamaguchi *et al.*, 1993 [275]

*please note: D.H. Hunneman, A cautionary note on phthalate esters of *Cryptotaenia canadensis*, *Tetrahedron Lett.*, **1968**, 1743-1743.

** not identified isomers ****DINP-2 are often produced as a mixture of isomers reported in 2011 to be composed of approx. 10% n-nonyl, 35-40 % methyloctyl, 40-45 % dimethylheptyl and 5-10 % methylethylhexyl (ECPI 2011b, ECHA 2012). Those manuscripts that describe the isolation of di-isononyl phthalates identify the molecules by GC/MS, so it may be reasonable to assume that these are mixtures of isomers if the phthalates are of anthropogenic origin. *****structure not conclusive from the paper ******isomer not formally specified *******authors noted that there was no certainty as to the origin of the compound [x]incompletely defined substance

(ECHA 2012) COWI, IOM Consulting and AMEC, Evaluation of new scientific evidence concerning the restrictions on DINP and DIDP contained in entry 52 of annex XVII to regulation (EC) NO 1907/2006 (REACH), final report volumes of DINP and DIDP, ECHA report, 2012; Accessed 14 April 2020 at: https://echa.europa.eu/documents/10162/a35fa99b-ed8f-4451-a4d5-f012e9ba69c7.

DIDP Information Centre, DINP Information Centre and DPHP Information Centre. The European Council for Plasticisers and Intermediates (ECPI). Accessed 14 April 2020 at: http://www.didp-facts.com/ , http://www.dinp-facts.com/ and http://www.dphp-facts.com/

Dialkyl phthalates are initially metabolized to monoalkyl phthalates by a number of microorganisms [104], and it has been realized that in the digestive lumen and liver of fish, monoalkyl phthalates (MPA) may also be produced from dialkyl phthalates [105]. This leads to 913 ± 885 ng/g MPA in European eel (*Anguilla anguilla*) muscles, collected in two French lagoons in the Mediterranean Sea [105], to 0.54 ng/g for benzyl phthalate (MBzP, **24**) to 82 ng/g for n-butyl phthalate (MnBP, **25**) in the muscles of juvenile Shiner Perch (*Cymatogaster aggregata*) [106] and to 0.24–1.1 ng/g for ethylhexyl phthalate (MEHP, **26**, 6.63–60.9 ng/g for MnBP (**25**) in the white-spotted greenling (*Hexagrammos stelleri*) [107]. In these cases again, the substrate phthalates will be of anthropogenic origin. Monoalkyl phthalates such as MEHP (**26**) and MnBP (**25**) have been isolated from a number of bacteria, algae and fungi, but also from terrestrial plants (Table **2**). Monoalkyl phthalates are being used as biomarkers for the original presence of dialkyl phthalates in organisms. The question remains in how far certain occurrences of phthalates in natural organisms indicate that they are natural products of these organisms. Table **2** shows a selection of reports of phthalates found in various organisms, especially in plants, bacteria, and fungi that do not specifically mention a possible anthropogenic origin of the phthalates. Of the 26 industrially most produced phthalates, only of diisoundecyl-, diisotridecyl- and of diallyl phthalate (**3**), no reports could be found regarding their isolation as products from plants. Interestingly, larger phthalates such as diisotridecyl phthalate, which is used in heat-resistant cables, have not been reported from plant isolates, either, yet. On the other hand, it would have been interesting to find the isolation of dialkyl phthalates that are known not to have been synthesized industrially. This data is hard to come by. Thus, it has been mentioned that one sign that bis(2-methylheptyl) phthalate were produced by *Hypericum hyssopifolium* (Guttiferae) itself, was that the compound was not used in the chemical industry [102]. It must be noted, however, that two patents existed for the production and use of the compounds at that time, one by BASF and one by Casio Computer Co [103].

It is interesting to screen the frequency of articles reporting on the isolation of phthalates with one short and one long alkyl chain, which is not that frequently found as additives in consumer products. These would include methyl propyl phthalate (**57**), *n*-butyl methyl phthalate (**58**), methyl *n*-pentyl phthalate (**59**), 2-ethylhexyl methyl phthalate (**60**) and the corresponding alkyl ethyl phthalates (Fig. **6**). The interesting finding is that quite a few reports of isolation of these “mis-matched”, non-symmetric, less produced phthalates from different organisms exist [108]. n-Butyl n-tetradecyl phthalate (**61**) was isolated from the leaves of *Urtica dioica* L [109]. together with a number of other compounds of anthropogenic origin such as di-n-butylphthalate (DnBP, **5**), di-2-ethylhexylphthalate (DEHP, **9**), tributyl phosphate (**55**), and bis(2-ethylhexyl)maleate (**56**), all used as plasticizers, sealants or hydraulic fluids. Ethyl methyl phthalate (EMP, **23**) was found in the stems of thorn apple [*Datura stramonium* L.] [110], in Italian thistle [*Carduus pycnocephalus* L.] [111], and dyer’s woad [*Isatis indigotica*] [112], among other plants. Research has shown that primary biodegradation of DEP mostly follows two paths, namely firstly the hydrolysis to monoethyl phthalate (MEP, **62**) and then to phthalic acid (PA, **63**) and secondly the de-methylation and trans-esterification to form ethyl methyl phthalate (EMP, **23**). These pathways have been shown to operate in *Pseudomonas sp*. DNE-S1 [113] and in *Sphingobium yanoikuyae* SHJ [114]. Enzymatic *trans*-esterification in natural organisms of industrial phthalates to mixed phthalates should be considered but has not been studied, to the best of the author’s knowledge. Finally, phthalic acid has been found in a number of plant extracts, such as in the ethyl acetate extract of *Bridelia ovata* [115] and ethanolic extracts of licorice (*Glycyrrhiza glabra*) leaves [116], sometimes in concert with phthalates [117]. It must be noted, however, that phthalic acid (**63**) also can derive from the oxidation of naphthalenes as VOCs in the atmosphere. On the other hand, terephthalic acid (**65**) (see below) can derive from the burning of plastic, while 1,2,4-benzenetricarboxylic acid (**64**) can originate from the oxidation of polycyclic aromatic hydrocarbons (PAHs). Thus, phthalic acid, as well as terephthalic acid (65) and 1,2,4-benzenetricarboxylic acid (64), have been found residing on $PM_{2.5}$ in the atmosphere (eg., at a max. of 73.2 ng/m^3 collected air space over Nanhai, China; 178.5 ng/m^3; and 43.4 ng/m^3, respectively) [118].

As mentioned above, terephthalates, trimellitates and ring-hydrogenated analogs of phthalates, *i.e.*, cyclohexane-1,2-dicarboxylates, have partially replaced phthalates as plasticizers in recent times, and they have started to appear in the environment in different concentrations. Thus, humans are equally exposed to terephthalates as has been shown in a recent German study on phthalate content in urine samples from 1999 to 2017, which indicated that the human exposure to para-phthalates (terephthalates) continues to grow [119] as these are replacing the phthalates as less regulated plasticizers. Here, the author tried to find whether this is also reflected in their isolation from natural sources. Indeed, reports on the isolation of terephthalates, especially from plant sources, could be found (Table **3**), as could be on the isolation of isophthalates (dialkyl 1,3-phthalates, Table **4**). Isophthalates in the form of ethylene terephthalate-isophthalate copolymers have been used in food packaging films, but have also been formulated as diluents in polymers such as polyethylene terephthalates [120]. Benzene-1,3-dicarboxylic acid (isophthalic acid, **66**) has been isolated from a number of plants. Typical isolations have been reported from the essential oil of *Dendrobium nobile* [121], and stems of cultivated *Dendrobium officinale*, and *Dendrobium huoshanense* [122] (Orchidaceae), from the air-dried parts of the whole plant *Swertia angustifolia* (Gentianaceae) [123], from the leaves of *Cerbera manghas* (sea mango, Apocynaceae) [124], and from the culture filtrate of the yeast *Candida tropicalis* [125]. In addition, ring-substituted isophthalic acids have been found, such as 2-acetyl-5-hydroxy-4-methoxyisophthalic acid (**67**, Fig. **6**) in the fungus *Talaromyces flavus* (Trichocomaceae) [126]. Few examples of the isolation of trimellitic acid esters as natural products could be located (Table **4**), even though these also had been forwarded as additives to agrochemical powder preparations [127] such as to fertilizers [128]. Moreover, to date, no report could be found of the isolation of diisononyl cyclohexane-1,2-dicarboxylate from a plant or other organism as a natural product.

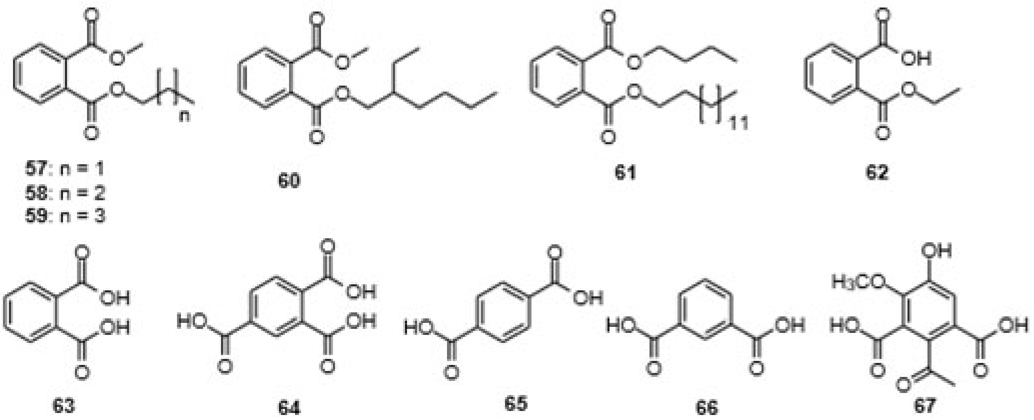

Fig. (6). Non-symmetric phthalates **57-61**, ethyl phthalate **62**, benzenedicarboxylic and tricarboxylic acids **63-67**.

Table 3. Isolation of terephthalates from natural sources (organisms).

Terephthalate	Organism Source	Description of Organism	Extracted Part of the Organism	Identification Method of the Terephthalate	Region/Location	Reference
Bis-(2-ethylhexyl)-terephthalate (**10**)	*Melodinus fusiformis*	Plant (*Apocynaceae*)	leaf, twig	GC/MS	China	D. Wang *et al*, 2012 [198]
Bis-(2-ethylhexyl)-terephthalate (**10**)	*Grewia lasiocarpa E. Mey. ex Harv.*	Evergreen shrub		GC/MS	Umdoni Trust Park, KwaZulu-Natal, South Africa.	N. Akwu *et al.*, 2019 [277]
Bis-(2-ethylhexyl)-terephthalate (**10**)	*Uncaria rhynchophylla*	Plant (Cat's claw herb)		NMR, MS	China (market purchased material)	Y.-L. Wang *et al.*, 2018 [231]
Bis-(2-ethylhexyl)-terephthalate (**10**)	*Penicillium griseofulvum*	Marine fungus			China	Y. Xu *et al.*, 2015 [278]

Terephthalate	Organism Source	Description of Organism	Extracted Part of the Organism	Identification Method of the Terephthalate	Region/Location	Reference
Bis-(2-ethylhexyl)-terephthalate (**10**)	*Alnus nitida*	West Himalayan alder	stem bark	GC/MS	Swat, Pakistan	M. Sajid *et al.*, 2017 [201]
Di-n-butyl terephthalate (**4**)	*Codonopsis thalictrifolia wall. var. mollis*	Soft bonnet bellflower		MS	China	J. Jing *et al.*, 2013 [279]
Di-n-butyl terephthalate (**4**)	*Semiaquilegia adoxoides*	Flowering plant (Ranunculaceae)	roots	NMR	China	N. Feng *et al.*, 2006 [280]
Di-n-butyl terephthalate (**4**)	*Leucas zeylanica*	Ceylon slitwort (Lamiaceae)		NMR, incl. 2D-NMR, MS	Haikou, China	N. Nidhal *et al.*, 2020 [232]
Di-n-butyl terephthalate (**4**)	*Dalbergia cochinchinensis*	Thailand rosewood (Fabaceae)		^{1}H NMR, ^{13}C NMR	Fangchenggang, Guangxi, China	R. Liu *et al.*, 2015 [199]
Di-n-butyl terephthalate (**4**)	*Melodinus hemsleyanus*	Plant (*Apocynaceae*)	leaf, twig	MS	China	J. Zhang *et al.*, 2013 [281]
Di-n-butyl terephthalate (**4**)	*Incarvillea younghusbandii sprague*	Bignoniaceae			China	L. Shen *et al.*, 2012 [282]
Di-n-butyl terephthalate (**4**)	*Dolomiaea souliei*	Flowering plant (Asteraceae)			China	H. Wei *et al.*, 2012 [233]
Di-n-butyl terephthalate (**4**)	*Typhonium giganteum Engl.*	Chinese aroid	essential oil		China	G. Peng, *et al.*, 2010 [283]
Di-n-butyl terephthalate (**4**)	*Gynura divaricata*	Flowering medicinal plant (Asteraceae)	aerial parts		China	L. Chen *et al.*, 2010 [284]
Di-n-butyl terephthalate (**4**)	*Mosla chinensis*	Plant (Lamiaceae)			China	H. Liu *et al.*, 2010 [285]
Diethyl terephthalate (**8**)	*Indigofera bungeana*	Plant (Leguminosae)		GC/MS	China	W. Tian *et al.*, 2006 [286]
Diethyl terephthalate (**8**)	*Mangifera indica*	Plant (Anacardiaceae)		NMR, MS	Yunnan, China	H. Jiang *et al.*, 2019 [287]
Diisobutyl terephthalate (**29**)	*Radix paeoniae rubra (Paeonia lactiflora Pallas and Paeonia veitchii Lynch)*	Medicinal herb from perennial flowers (*Paeoniacea*)		GC/MS	China	X. Feng *et al.*, 2014 [288]
Diisobutyl terephthalate (**29**)	*Durian fruit (peel)*	tree	volatile constituents of fruit peel	GC/MS	China	B. Zhang *et al.*, 2012 [192]
Di-n-octyl terephthalate (**30**)	*Elsholtzia communis*	Lamiaceae	essential oil	GC/MS	China	Y.L Lu *et al.*, 2013 [289]
*Dimethyl terephthalate** (**18**)	*Uncaria gambir (Roxb.)*	Flowering plant (Rubiaceae)	leaf	GC/MS	West Sumatra, Indonesia	D. Nandika *et al.*, 2019 [290]
*Dimethyl terephthalate** (**18**)	*Myristica argentea*	Papua nutmeg (Myristicaceae)		NMR	China	J. Shi *et al.*, 2010 [291]
*Dimethyl terephthalate** (**18**)	*Elsholtzia communis*	Lamiaceae	essential oil	GC/MS	China	Y.L Lu *et al.*, 2013 [289]
*Dimethyl terephthalate** (**18**)	*Syzygium cumini*	Malabar plum (Myrtaceae)	bark	GC/MS	Madhya Pradesh, India	Mehta, B.K. *et al.*, 2012 [211]
*Dimethyl terephthalate** (**18**)	*Goniothalamus tapis Miq*	(Annonaceae)	bark		Malaysia	B. Moharam *et al.*, 2012 [292]

Terephthalate	Organism Source	Description of Organism	Extracted Part of the Organism	Identification Method of the Terephthalate	Region/Location	Reference
*Dimethyl terephthalate** (**18**)	*Goniothalamus uvaroides King*	(Annonaceae)	bark		Malaysia	B. Moharam *et al.*, 2012 [292]
*Dimethyl terephthalate** (**18**)	Phoma betae Phoma betae Phoma betae *Phoma betae (Pleospora betae)*	Endophytic fungus plant pathogen	fermentation extract		State of São Paulo, Brazil	M.B.C. Gallo *et al.*, 2009 [293]
[4-(Methoxycarbonyl)-phenyl]methyl methyl terephthalate (**31**)	*Alnus nitida*	West Himalayan alder	stem bark	GC/MS	Swat, Pakistan	M. Sajid *et al.*, 2017 [201]

* as residual starting material used in the polymer preparation

Table 4. Isolation of isophthalates and trimellitates from natural sources (organisms).

Isophthalate and Trimellitate	Organism Source	Description of Organism	Extracted Part of the Organism	Identification Method of the Isophthalate	Region/Location	Reference
Tri(2-ethylhexyl) trimellitate (**45**)	*Marine bacteria from the sponge Acanthella cavernosa*		bacteria	GC/MS	Lombok, Indonesia	T. Murniasih *et al.*, 2016 [294]
Tri(2-ethylhexyl) trimellitate (**45**)	*Moringa oleifera*	Drumstick tree (Moringaceae)	root	GC/MS	HEJICCBS garden, University of Karachi, Pakistan	S. Faizi *et al.*, 2014 [206]
Di-n-butyl isophthalate (**46**)	*Butia yatay*	Yatay palm	Essential oil of the fruit	GC/MS	China	Z.G. Lu *et al.*, 2008 [295]
Di-n-butyl isophthalate (**46**)	*Elsholtxia fruticosa* Rehd	(Lamiaceae)	Essential oil	GC/MS	China	S.Z. Zheng *et al.*, 2004 [296]
Di(ethylhexyl) isophthalate (**48**)	*Cordia myxa*	Flowering plant (Boraginaceae)	leaf	GC/MS	Enrekang, South Sulawesi, Indonesia	A. Najib *et al.*, 2019 [297]
Di(ethylhexyl) isophthalate (**48**)	*Elaeagnus angustifolia*	Russian olive (Elaeagnaceae)	Volatile oil of the flower	GC/MS	Xinjiang, China	R. Aynur *et al.*, 2015 [298]
Di(ethylhexyl) isophthalate (**48**)	*Capparis spinosa*	Caper bush (Capparaceae)	Seed oil	GC/MS	Velenjak, Tehran, Iran	K.M. Ara *et al.*, 2014 [299]
Dioctyl isophthalate (**47**)	*Citrus maxima (Burm.) Merr. cv. Liangpin Yu*	Liangpin pomelo	Pulp and skin (exocarp)	GC/MS	Market, China	X. Bai *et al.*, 2015 [300]
Dioctyl isophthalate (**47**)	*Zanthoxylum schinifolium*	Sichuan pepper		GC/MS	Market, China	X. Bai *et al.*, 2015 [300]
Dioctyl isophthalate (**47**)	*Pinctada martensii*	Pearl oyster	Meat	GC/MS	China	J. Liu *et al.*, 2011 [301]
Dimethyl isophthalate (**122**)	*Syzygium cumini*	Malabar plum (Myrtaceae)	bark	GC/MS	Ujjain (Madhya Pradesh), India	B.K. Mehta *et al.*, 2012 [211]

1.5. Uncommon Phthalates Isolated from Organisms as an Indication that These are Natural Products and not Products of Anthropogenic Origin

2-Methyl-, 2-ethyl, and 2-propylalkyl phthalates such as compounds **9**, **21** **36**, and **43** exhibit stereocenter(s), where it must be noted that industrial phthalates are produced as stereoisomeric mixtures from the racemic alcohols. A number of papers have reported on the isolation of enantiopure or at least enantio-enriched phthalates [129, 130], indicating the natural origin of these phthalates. In the isolation of bis(2*S*-methylheptyl) phthalate (***S*-36**) from the evergreen perennial plant *Ajuga bracteosa*, the authors did not forward any analytical result that indicated that the isolated substance was enantiopure or indeed chiral. The structure presented in the paper is that of the *meso* form of the compound, (*R*/*S*)-bis(2-methylheptyl) phthalate (**36**) [129], but the isolation of the compound could potentially be that of a mixture of stereoisomers. Different is the case of the isolation of bis(2*S*-methylheptyl) phthalate from *Galinsoga parviflora*, a herbaceous plant of the Asteraceae family, where the isolated compound shows a specific optical rotation $[\alpha]_D^{23}$ of 193.5° (c

= 0.075M, MeOH). Here, the question remains as to whether selective enzymatic hydrolysis of a mixture of bis(2-methylheptyl) phthalate stereoisomers has led to (*R*/*S*)-bis(2-methylheptyl) phthalate (**36**) as the one remaining dialkyl phthalate or whether the phthalate as a whole has been biosynthetically created (Fig. **7**).

Undoubtedly, there are phthalates that have been isolated from organisms that thus far have had no place in the industry. One such is kurraminate [bis(2-hydroxymethylnonadec-3*E*-enyl) phthalate] (**68**) isolated from flowering plant *Nepeta kurramensis* at Khyber Pakhtunkhwa, Pakistan [131], along with known bis(2-ethyleicosyl) phthalate (**33**), which was also isolated from *Phyllanthus muellerianus* in West Africa [132]. Also, **33** is not produced industrially. Bis(7-acetoxy-2-ethyl-5-methylheptyl) phthalate (**69**) has been isolated from translucent honeysuckle (*Lonicera quinquelocularis*). This terminally hydroxylated phthalate, which possesses four stereocenters, not discussed by the authors, again is apparently not of anthropogenic origin [133, 134]. The phthalate has been isolated together with the common anthropogenic phthalates DEHP (**9**) and di-*n*-octyl phthalate (**20**). 69 shows an acetylcholinesterase (AChE) and butyrylcholinesterase (BChE) inhibitory activity with IC_{50} of 1.65 and 5.98 μM.

One of the most compelling examples that phthalates can indeed be of natural origin is the isolation of a row of diethylene glycol phthalate ester oligomers from the marine-derived fungus *Cochliobolus lunatus* [135], which was subjected to epigenetic manipulation with the DNA transferase inhibitor 5-azacytidine (**70**). This led to the isolation of the seven diethylene glycol phthalate esters **72**, **75**-**79**, and **82** (Fig. **9**), in addition to the known compounds **71**, **74**, **80**, and **81** (Figs. **8** and **9**). The compounds have been analyzed by NMR spectroscopic methods, and there is no question as to their identity. The fungus itself was obtained from a piece of fresh tissue from the inner part of the sea anemone *Palythoa haddoni*, collected from the Weizhou coral reef in the South China Sea [135]. The linear polyether motif is not common in nature. The central building block, bis[2-(2-hydroxyethoxy) ethyl] phthalate (**71**), as an additive in polyurethanes, however, has been subject to a large number of patents [136, 137], appearing in patents as early as 1957 [138], and of directed synthesis [139]. [2-(2-Hydroxyethoxy)ethyl] methyl phthalate (**72**) had not been reported previously, but [2-(2-hydroxyethoxy)ethyl] phthalate (**73**) has been covered in a number of patents and also phthalate **74** has appeared in a patent [140].

A further strong indication that certain phthalates can be of natural origin comes from studies of C.Y. Chen *et al.*, who showed with a ^{14}C inclusion experiment that the red algae *Bangia atropurpurea* can *de novo* synthesize DEHP (**9**) and DnBP (**5**) [141]. *B. atropurpurea* filaments were cultured in a medium containing $NaH^{14}CO_3$. After two weeks, the radioactivity of DEHP (**9**) and DnBP (**5**) fractionated by HPLC from cultured filaments was analyzed, where single peak fractions of DEHP (160.00 cpm) and DnBP (4786.67 cpm) were found to have significantly higher radioactivities than the background (28.00 cpm) [141]. It is not clear, though, whether carbon-14 isotope was built into the structures indiscriminately or whether, for instance, it was only built into the alkyl chain of the esters.

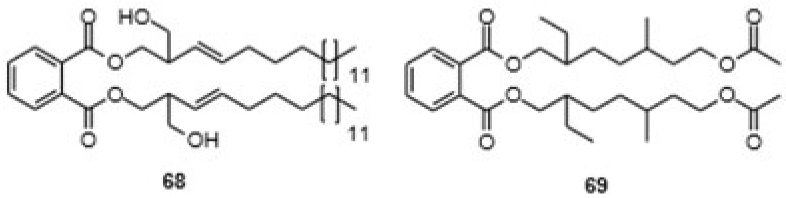

Fig. (7). Phthalates **68** and **69**, two phthalates that are not produced industrially.

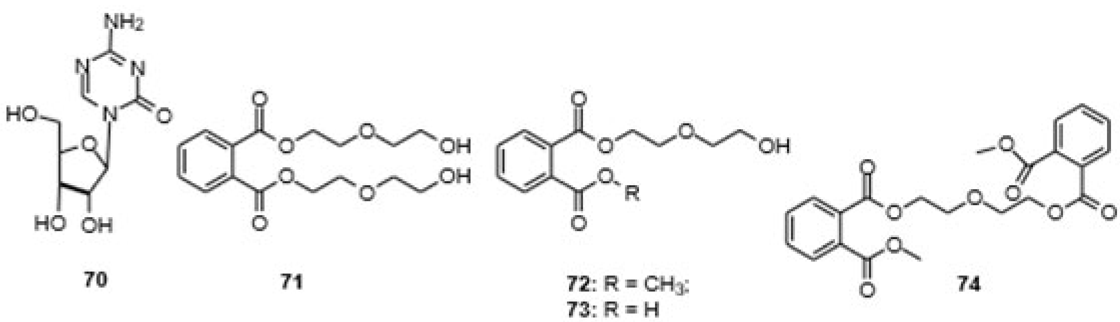

Fig. (8). 5-Azacytidine (**70**), bis[2-(2-hydroxyethoxy)ethyl] phthalate (**71**), [2-(2-hydroxyethoxy)ethyl] methyl phthalate (**72**), [2-(2-hydroxyethoxy) ethyl] phthalate (**73**) and bis-phthalate **74** [135].

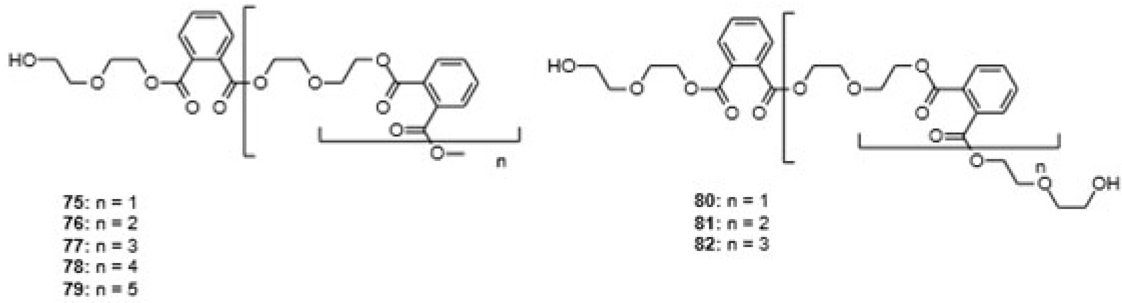

Fig. (9). Diethylene glycol phthalate ester oligomers isolated from the marine-derived fungus *Cochliobolus lunatus* [135].

Looking at many of the known biosynthetic pathways involving aromatic structures such as the phenylpropanoid pathway, it is evident that these rarely give rise to aromatic substances with more than one carboxylic acid group substituting the arene unit. In fact, it is very uncommon to find an aromatic natural compound with two electron-withdrawing groups that is not an intermediate. More often than not, electron-donating hydroxyl, alkoxyl or amino groups are in evidence in naturally occurring aromatic compounds such as in the aromatic building blocks of plant lignins in the form of ferulates **83**, hydroxycinnamates **84**, with coniferyl alcohol (**85**) as a building block, in aromatic alkaloids such as bufotenin (**86**), flavonoids such as 2-phenylchromen-4-one (**87**), chalcones such as xanthohumol (**88**) and amino acids such tyrosine (**89**) and tryptophane (**90**) (Fig. **10**).

C. Tian *et al.* showed that DnBP (**5**) is produced by naturally occurring filamentous fungi *Penicillium lanosum* PTN121, *Trichoderma asperellum* PTN7 and *Aspergillus niger* PTN42, cultured in an artificial medium [142]. Using an enzyme excreted by the fungi, the authors were able to enzymatically produce DnBP (**5**) under cell-free conditions from D-glucose (**91**) alone, from D-glucose and 1-butanol, from protocatechuic acid (**94**) and 1-butanol, and from phthalic acid (**63**) and 1-butanol (Fig. **11**). This result indicates that DnBP (**5**) could be produced by the shikimic acid pathway [142], although the mechanism of the transformation of protocatechuic acid (**94**) to phthalic acid (**63**) is not clear, yet (Figs. **11**-**13**).

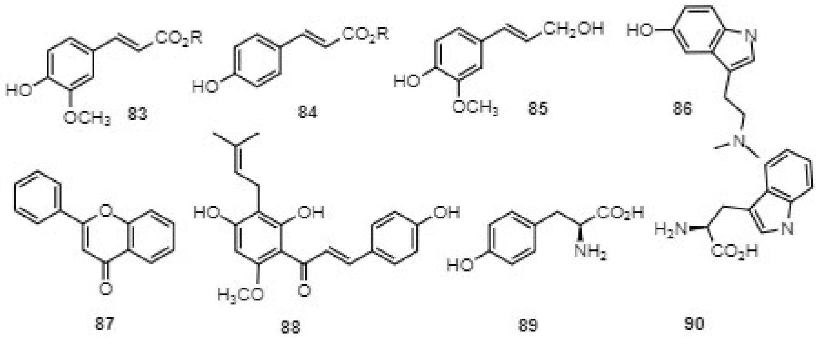

Fig. (10). Typical natural products with an aromatic subunit.

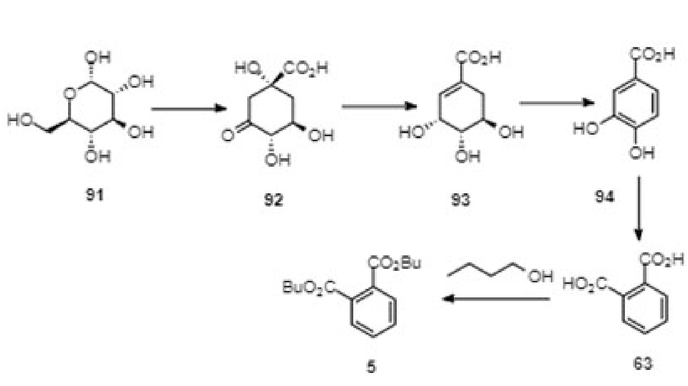

Fig. (11). Proposed pathway from glucose (**91**) to dibutyl phthalate (**5**) [142].

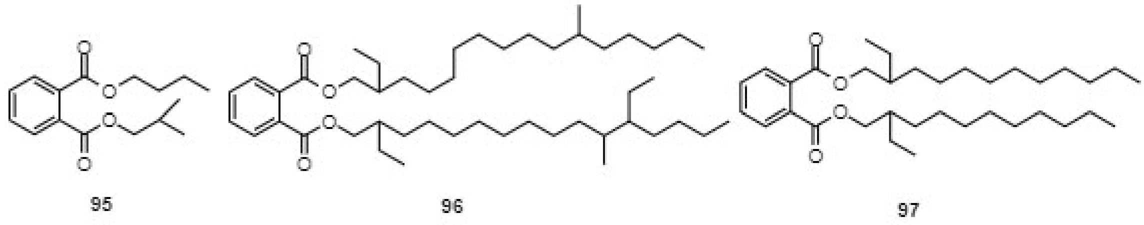

Fig. (12). Butyl *iso*butyl phthalate (**95**) and 2,12-diethyl-11-methylhexadecyl 2-ethyl-11-methylhexadecyl phthalate (**96**) and 2-ethyldecyl 2-ethylundecyl phthalate (**97**), isolated from the seahorse *Hippocampus Kuda* Bleeler [152].

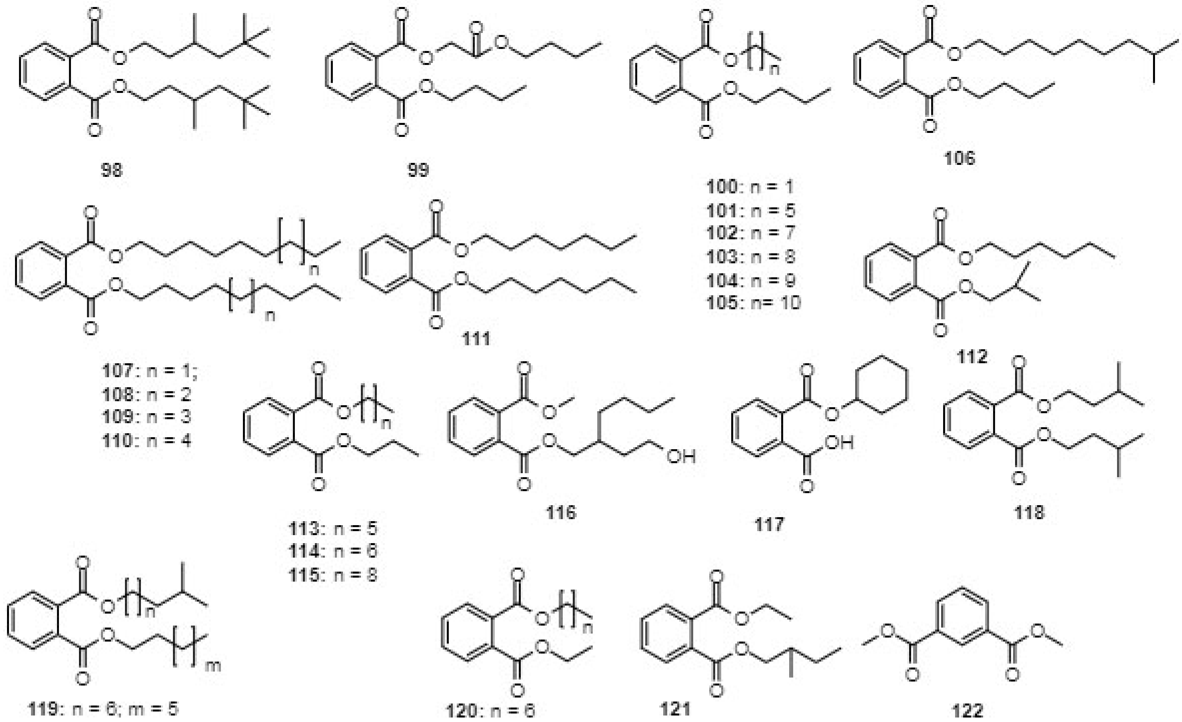

Fig. (13). Phthalates introduced in the tables.

1.6. Biological Activities of Phthalates Isolated from Organisms and Comparison to Activities and Hazard Assessment Associated with Industrial Phthalates

The biological assessment carried out on phthalates isolated from plants as potential natural products is quite different from that carried out on phthalates as industrial plasticizers. In the former, phthalates have been screened for their potentially benevolent effects such as antitumour compounds, antimicrobial products and larvicidal agents. In the latter, potential health and environmental risks associated with the compounds have been assessed, also for regulative purposes, which results, for instance, in the testing of these compounds for their hormonal activity. Both of these biological assessment series are nicely complementary.

In many reports of the isolation of phthalates from natural sources, the authors have tested plant extracts containing, apart from the phthalates, a plethora of other components. In these cases, it is difficult to tie the respective biological activity of the extract to the phthalate ingredient. However, there are also a number of reports of testing the biological activity of isolated phthalates collected from natural organisms. In this regard, bis(2-ethylhexyl)phthalate (**9**) isolated from the flower of *Procera gigantea* was found to be active against the gram-positive bacteria *Staphylococcus aureus*, *Bacillus subtilis*, *Streptococcus equosemens* and *Sarcina lutea* [143, 144] and against the gram-negative bacteria *Closteridium perfringens*, *Escherchia coli*, *Pseudomonas aeruginosa*, *Shigella sonnei*, *Shigella shiga* and *Shigella dysenteriae* [143, 144]. The compound was found to inactive against *Bacillus megaterium* [143]. Bis(2-ethylhexyl)phthalate (**9**) showed activity against the fungus *Aspergillus flavus* as well. *Aspergillus fumigatus*, *Aspergillus niger*, and *Fusarium sp.* were found to be resistant against the compound [143]. Not all biological activity tests have led to unanimous results, nevertheless a more detailed compilation of the antimicrobial test results of isolated and purified phthalates from the literature can be found in Table **5**.

Both di-*n*-hexyl phthalate (**14**) and bis(2-propylheptyl) phthalate (**21**), isolated from the rhizopheric soil of the tobacco plant, have been found to have allelochemical properties *versus* lettuce (*Lactuca sativa*). Also, they showed autotoxic effects on the flue-cured tobacco plant itself [145] (Table **6**). Allelochemical properties of phthalates are not unusual. Thus, dimethyl phthalate has been found to be a typical allelochemical of the perennial invasive plant *Solidago canadensis* (Canadian goldenrod) [146], which leads to delayed seed germination and reduced seedling growth of a number of plants such as wheat and mulberry. Dibutyl phthalate (DnBP, **5**) and diisobutyl phthalate (DIBP, **12**) were detected in high concentrations in naturally decomposed cotton stalk extracts. These strongly inhibited the cotton seedling growth in a bioassay, indicating autotoxic effects [147]. However, it must be noted that in all the cases above, it was not ascertained that the phthalates were indeed authentic natural products of the plants; also, it must be observed that such allelopathic effects should be taken into account when applying plastic mulch in plant production.

M. Uyeda *et al.* showed that DEHP (**9**) aggregates the gram-negative bacteria *Proteus vulgaris* and *Serratia marcescens* as well as HeLa cells [148]. Butyl *iso*butyl phthalate (**95**), this time isolated from the brown alga *Laminaria japonica* (*Saccharina japonica)*, showed non-competitive inhibitory *in vitro* activity against α-glucosidase [149], toted at one time as a possible drug to help treat type II diabetes. Di-*n*-octyl phthalate (**20**) found in the plant *Pachygone ovata* (Poir.) Miers ex Hook. F. & Thomson is most likely of anthropogenic origin. The tests conducted with the isolated compound once again show the acute biological activity of such environmental pollutants. Di-*n*-octyl phthalate (**20**) was found to be cytotoxic towards MCF-7 breast cancer cells with an IC_{50} of 42.5 μg/mL. The compound was found to upregulate CASPASEs 3 and 9 and downregulate BCL2 gene expression, inducing BCL2 regulated apoptosis [150]. Dioctyl phthalate, here isolated from *Nigella glandulifera* Freyn, was also identified as a tyrosinase inhibitor, which leads to an inhibition of melanogenesis [151]. Other phthalates were found to be cytotoxic to MCF-7 (see Table **7**).

Finally, the four phthalates, bis(2-ethylheptyl) phthalate (**35**), 2,12-diethyl-11-methylhexadecyl 2-ethyl-11-methylhexadecyl phthalate (**96**), 2-ethyldecyl 2-ethylundecyl phthalate (**97**), and bis(2-ethyldodecyl) phthalate (**34**) isolated from the seahorse *Hippocampus Kuda* Bleeler, showed dose-dependent cathepsin B inhibition activities with IC_{50} values of 0.13 mM (1), 0.21 mM (2), 0.18 mM (3), and 0.29 mM (4), respectively [152]. Cathepsin B is a lysosomal cysteine protease of the papain family, which functions in intracellular protein catabolism.

Table 5. Antimicrobial activity of purified phthalates isolated from natural sources.

Antimicrobial Activity	Phthalate	Organism Source	Part Extracted	Reference
Staphylococcus aureus	*Bis(2-ethylhexylphthalate)* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
S. aureus	*Bis(2-ethylhexylphthalate)* (**9**)	*Streptomyces mirabilis*	broth extract	M. El-Sayed, 2012 [144]
S. aureus	*Bis(2-ethylhexylphthalate)* (**9**)	*Streptomyces sp. TN17*	broth extract	S. Smaoui *et al.*, 2011 [302]
S. aureus / MIC 32 μg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces bangladeshiensis*		M.A.A. Al-Bari *et al.*, 2006 [303]
S. aureus 209P FDA /MIC >300 μg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces nasri* H35	Broth extract	M.Y. El-Naggar, 1997 [214]
S. aureus NRRL B 313	*Bis(2-ethylhexylphthalate)* (**9**)	*Streptomyces* SB9	Broth extract	D. Lyutskanova *et al.*, 2009 [304]
S. aureus MTCC 96/ MIC 18.75 μg/mL	*Bis(2-ethylhexylphthalate)* (**9**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
S. aureus MTCC 96/ MIC 37.5 μg/mL	*Di-n-butyl phthalate* (**5**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
Staphylococcus epidermis MTC 435 /MIC 9.37 μg/mL	*Bis(2-ethylhexylphthalate)* (**9**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
Staphylococcus epidermis MTC 435 /MIC 9.37 μg/mL	*Bis(2-ethylhexylphthalate)* (**9**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
Acinetobacter johnsonii ATCC17909	*Bis(2-ethylhexylphthalate)* (**9**)	*Streptomyces* SB9	Broth extract	D. Lyutskanova *et al.*, 2009 [304]
Aeromonas hydrophila 2 μg/mL	*Bis(2-ethylhexylphthalate)* (**9**	*Streptomyces ruber EKH2*		K.M. Barakat and E.A. Beltagy, 2015 [305]
Bacillus mycoides DSMZ274 (resistant)	*Bis(2-ethylhexylphthalate)* (**9**)	*Streptomyces* SB9	Broth extract	D. Lyutskanova *et al.*, 2009 [304]
Bacillus subtilis MIC 32 μg/mL	*Bis(2-ethylhexylphthalate)* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
B. subtilis	*Bis(2-ethylhexylphthalate)* (**9**)	*Vicia villosa*	shoots	M.T. Islam *et al.*, 2013 [181]
B. subtilis	*Bis(2-ethylhexylphthalate)* (**9**)	*Streptomyces mirabilis*	broth extract	M. El-Sayed, 2012 [144]
B. subtilis	*Diethyl phthalate* (**7**)	*Vicia villosa*	shoots	M.T. Islam *et al.*, 2013 [181]
B. subtilis MTCC 441 /MIC 37.5 μg/mL	*Bis(2-ethylhexylphthalate)* (**9**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]

Antimicrobial Activity	Phthalate	Organism Source	Part Extracted	Reference
B. subtilis MTCC 441 /MIC 18.75 µg/mL	*Di-n-butyl phthalate* (**5**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
B. subtilis 6633 ATCC /MIC >400 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces nasri* H35	Broth extract	M.Y. El-Naggar, 1997 [214]
B. subtilis 6633	*Bis(2-ethylhexylphthalate)* (**9**)	*Streptomyces* SB9	Broth extract	D. Lyutskanova *et al.*, 2009 [304]
B. subtilis 6633 / MIC 84 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*		N. Roy *et al.*, 2006 [217]
B. subtilis / MIC 16 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces bangladeshiensis*		M.A.A. Al-Bari *et al.*, 2006 [303]
Bacillus cereus PX MU-COB / MIC >300 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces nasri* H35	Broth extract	M.Y. El-Naggar, 1997 [214]
Bacillus megatherium (resistant)	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
Bacillus megatherium NRRL 1353895	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces* SB9	Broth extract	D. Lyutskanova *et al.*, 2009 [304]
Closteridium perfringens	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces mirabilis*	broth extract	M. El-Sayed, 2012 [144]
Salmonella typhi 653 / MIC 76 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*		N. Roy *et al.*, 2006 [217]
S. typhi / MIC 16 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces bangladeshiensis*		M.A.A. Al-Bari *et al.*, 2006 [303]
Sarcina lutea / MIC 32 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
Sarcina lutea ATCC9341	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces* SB9	Broth extract	D. Lyutskanova *et al.*, 2009 [304]
Edwardsiella tarda 8 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces ruber EKH2*		K.M. Barakat and E.A. Beltagy, 2015 [305]
Escherchia coli	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
E. coli	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces mirabilis*	broth extract	M. El-Sayed, 2012 [144]
E. coli ATCC 8739 (resistant)	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces sp. TN17*	broth extract	S. Smaoui *et al.*, 2011 [302]
E. coli MTCC 443 / MIC 37.5 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
E. coli MTCC 443 / MIC 37.5 µg/mL	*Di-n-butyl phthalate* (**5**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
E. coli 25922 / MIC 53 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006
Klebsiella pneumoniae (MTCC 618) / MIC 75 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
Klebsiella pneumoniae (MTCC 618) / MIC 75 µg/mL	*Di-n-butyl phthalate* (**5**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
Micrococcus luteus	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces sp. TN17*	broth extract	S. Smaoui *et al.*, 2011 [302]
Pseudomonas aeruginosa	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces mirabilis*	broth extract	M. El-Sayed, 2012 [144]
P. aeruginosa MTCC 741 / MIC 75 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
P. aeruginosa MTCC 741 / MIC 37.5 µg/mL	*Di-n-butyl phthalate* (**5**)	*Brevibacterium McBellneri*		M. Rajamanikyam *et al.*, 2017 [164]
P. aeruginosa 8 µg/mL	*Bis(2-ethylhexylphthalate)* (**9**	*Streptomyces ruber EKH2*	broth extract	K.M. Barakat and E.A. Beltagy, 2015 [305]
Pseudomonas fluores-cens / MIC >300 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces nasri* H35	broth extract	M.Y. El-Naggar, 1997 [214]
Shigella sonnei	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
Shigella shiga	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
Shigella dysenteriae	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
S. dysenteriae / MIC 32 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces bangladeshiensis*		M.A.A. Al-Bari *et al.*, 2006 [303]
Rhizobium vitis	*Bis(2-ethylhexyl) phthalate* (**9**)	*Vicia villosa*	shoots	M.T. Islam *et al.*, 2013 [181]
R. vitis	*Diethyl phthalate* (**7**)	*Vicia villosa*	shoots	M.T. Islam *et al.*, 2013 [181]
Streptococcus equosemens	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces mirabilis*	broth extract	M. El-Sayed, 2012 [144]
Vibrio ordalii	*Bis(2-ethylhexylphthalate)* (**9**	*Streptomyces ruber EKH2*	broth extract	K.M. Barakat and E.A. Beltagy, 2015 [305]

Antimicrobial Activity	Phthalate	Organism Source	Part Extracted	Reference
Aspergillus flavus	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
A. flavus (rel. resistant)	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces mirabilis*	broth extract	M. El-Sayed, 2012 [144]
A. flavus / MIC 128 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces bangladeshiensis*	broth extract	M.A.A. Al-Bari *et al.*, 2006 [303]
Aspergillus fumigatus (resistant)	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea* *Streptomyces mirabilis*	flower broth extract	M.R. Habib and M.R. Karim, 2009 [143] M. El-Sayed, 2012 [144]
A. fumigatus	*Di-n-butyl phthalate* (**5**)	*Streptomyces nasri* H35	Broth extract	M.Y. El-Naggar, 1997 [214]
Aspergillus niger (resistant)	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea* *Streptomyces mirabilis*	flower broth extract	M.R. Habib and M.R. Karim, 2009 [143] M. El-Sayed, 2012 [144]
A. niger 1781 / MIC 98 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]
A. niger / MIC 64 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces bangladeshiensis*	broth extract	M.A.A. Al-Bari *et al.*, 2006 [303]
Curvularia pallescens 403 / 117 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]
Fusarium sp.	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces sp. TN17*	broth extract	S. Smaoui *et al.*, 2011 [302]
Fusarium sp. (resistant)	*Bis(2-ethylhexyl) phthalate* (**9**)	*Calotropis gigantea*	flower	M.R. Habib and M.R. Karim, 2009 [143]
Trichosporon cutaneum R57	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces* SB9	broth extract	D. Lyutskanova *et al.*, 2009 [304]
Candida albicans	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces mirabilis*	broth extract	M. El-Sayed, 2012 [144]
C. albicans / MIC 64 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces bangladeshiensis*	broth extract	M.A.A. Al-Bari *et al.*, 2006 [303]
Candida tropicalis ATCC20336	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces* SB9	broth extract	D. Lyutskanova *et al.*, 2009 [304]
Saccharomyces cerevisiae (resistant)	*Di-n-butyl phthalate* (**5**)	*Streptomyces nasri* H35	broth extract	M.Y. El-Naggar, 1997 [214]
S. cerevisiae DSM70449	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces* SB9	broth extract	D. Lyutskanova *et al.*, 2009 [304]
S. cerevisiae 176 / MIC 92 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]

Table 6. Allelopathic properties of purified phthalates isolated from natural sources.

Affected Plant	Phthalate	Natural Source of the Phthalate	Source of the Phthalate	Reference
Lactuca sativa	*Di-n-hexyl phthalate* (**14**)	*Tobacco plant*	rhizopheric soil	X. Ren *et al.*, 2015 [145]
Tobacco plant (autotoxic)	*Di-n-hexyl phthalate* (**14**)	*Tobacco plant*	rhizopheric soil	X. Ren *et al.*, 2015 [145]
Lactuca sativa	*Bis(2-propylheptyl) phthalate* (**21**)	*Tobacco plant*	rhizopheric soil	X. Ren *et al.*, 2015 [145]
Tobacco plant (autotoxic)	*Bis(2-propylheptyl) phthalate* (**21**)	*Tobacco plant*	rhizopheric soil	X. Ren *et al.*, 2015 [145]

Table 7. Cytostatic activity of phthalates isolated from natural sources.

Cell Type and IC_{50} Value	Phthalate	Natural Source of the Phthalate	Extracted Part of the Organism	Reference
CHO (ATCC; CCL-61) IC_{50} = 36±8.6 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]
CHO (ATCC; CCL-61) IC_{50} = 193±5.4 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]
DU145 (ATCC; HTB-81) IC_{50} = 31.23±8.7 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]
DU145 (ATCC; HTB-81) IC_{50} = 33.46±7.7 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]
HEK293 (ATCC; CRL-1573) IC_{50} = 19.77±10 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]
MCF-7 (ATCC; HTB-22) IC_{50} = 32.43±3.6 µg/mL	*Di-n-butyl phthalate* (**5**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]
MCF-7 IC_{50} = 0.13 mM	*Di-n-octyl phthalate* (**20**)	*Pachygone ovata* (Poir.) Miers		L.E. Amalarasi and G.J. Jothi, 2019 [150]
MCF-7 (ATCC; HTB-22) IC_{50} = 46.55±0.1 µg/ml	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces albidoflavus*	broth extract	N. Roy *et al.*, 2006 [217]

Cell Type and IC_{50} Value	Phthalate	Natural Source of the Phthalate	Extracted Part of the Organism	Reference
MCF-7 IC_{50} = 69.2 µM	*Bis(2-methylheptyl) phthalate* (**36**)	*Phyllanthus pulcher*		G. Bagalkotkar, 2007 [177]
Toxicity against brine shrimp Artemia salina larvae LC_{50} = 2800 µg/mL	*Bis(2-ethylhexyl) phthalate* (**9**)	*Streptomyces ruber EKH2*	broth extract	K.M. Barakat and E.A. Beltagy, 2015 [305]

CONCLUSION

Phthalates have been isolated from a multitude of different natural sources. Oftentimes, the phthalates are isolated as a bouquet of different phthalates, sometimes in conjunction with siloxanes, which definitely are of anthropogenic origin. This tends to signalize that in most of the cases, the phthalates themselves are of anthropogenic origin. While it is known that phthalates can stem from contamination from laboratory equipment, most of the phthalates found in natural sources may originate from fertilizers, other agrochemicals, irrigation water, or by import through the atmosphere. On the other hand, there are a few phthalates found in nature that are not produced industrially. As these differ solely in their *O*-alkyl groups, it must be considered whether enzymatic esterification/trans-esterification, starting from anthropogenic phthalates, may play a role. Furthermore, few phthalates have been found in nature in which the aromatic core is substituted further. Nevertheless, it has been shown that carbon-14 is built into secreted phthalates by *B. atropurpurea* filaments when cultured in a medium containing $NaH^{14}CO_3$. While a detailed, clear, and plausible biogenetic route to phthalates, should they be natural products, has not yet been forwarded, it could be shown with a fungal enzyme that dibutyl phthalate could be produced from glucose, indicating that a natural shikimic acid pathway to phthalates may exist. As phthalates upon isolation from various sources were seen as natural products, many of the biological assays typically carried out on newly identified natural compounds were also performed on them, leading to the recognition of their antimicrobial activity. These tests nicely complement the mandatory tests carried out on them as plasticizers produced industrially on a large scale.

LIST OF ABBREVIATIONS

BBzP	=	*n*-Butyl benzyl phthalate (1)
BCP	=	*n*-Butyl cyclohexyl phthalate(2)
DAP	=	Diallyl phthalate(3)
DnBT	=	Di-*n*-butyl terephthalate(4)
DnBP	=	Di-*n*-butyl phthalate(5)
DBEP	=	Dibutoxy ethyl phthalate(6)
DEP	=	Diethyl phthalate (7)
DET	=	Diethyl terephthalate (8)
DEHP	=	Bis(2-ethylhexyl) phthalate (9)
DEHT	=	Di(2-ethylhexyl) terephthalate (10)
DcHP	=	Dicyclohexyl phthalate (11)
DiBP	=	Diisobutyl phthalate (12)
DIDP	=	Diisodecyl phthalate (13)
DIHP	=	Di-n-hexyl phthalate (14)
DINP	=	Diisononyl phthalate (15)
DIOP	=	Diisooctyl phthalate (16)
DMP	=	Dimethyl phthalate (17)
DMT	=	Dimethyl terephthalate (18)
DNPP	=	Dipentyl phthalate (diamyl phthalate)(19)
DnOP	=	Di-n-octyl phthalate (20)
DPHP	=	Bis(2-propylheptyl) phthalate (21)
DPP	=	Di-n-propyl phthalate (22)
EMP	=	Ethyl methyl phthalate (23)
HDPE	=	High density polyethene
LDPE	=	Low density polyethene
MBzP	=	Benzyl phthalate (**24**)
MnBP	=	n-Butyl phthalate (**25**)
MEHP	=	Ethylhexyl phthalate (**26**)
MnHP	=	n-Hexyl phthalate (**27**)
MnOP	=	n-Octyl phthalate (**28**)
MPA	=	Monoalkyl phthalate
MW	=	molecular weight
PVA	=	Polyvinyl acetate
PVC	=	Polyvinyl chloride

CONSENT FOR PUBLICATION

Not applicable.

STANDARDS OF REPORTING

PRISMA guidelines were followed in this study.

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CONFLICT OF INTEREST

The author declares no conflict of interest, financial or otherwise.

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