organics

Review

Aldehydes: What We Should Know About Them

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Abstract: From Egyptian mummies to the Chanel N° 5 perfume, aldehydes have been used for a long time and continue to impact our senses in a wide range of perfumes, foods, and beverages. Aldehydes represent one of the categories of volatile organic compounds (VOCs), which are categorized as chemicals with boiling points up to 260 °C and can be found in indoor environments in the gaseous phase. Because of their potential or known hazardous properties for humans, the World Health Organization (WHO)-Europe provided some guidelines that may prevent several health risks. Indeed, some aldehydes, reported to be risky for humans, have been retired from the market, such as butylphenyl methylpropional (BMHCA). The purpose of this review is to summarize the most important aldehydes found indoors and outdoors and analyse in depth the toxicological aspects of these compounds, whose presence in perfumes is often underestimated. In addition, the ingredients' synonyms that are reported in the literature for the same compound were unified in order to simplify their identification.

Keywords: BMHCA; volatile organic compounds; aldehydes; personal care products; 2-(4-*tert*-butylbenzyl)propionaldehyde

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1. Introduction

Flavours and fragrance chemicals are agents that may promptly stimulate the gustatory and olfactory receptors in the mouth and nose. They belong to the VOCs, among which aldehydes represent a particular group of potentially reactive organic compounds, due to the polarized carbon–oxygen double bond present in their structure [1], and include fatty aldehydes, such as hexanal, decanal, and octanal, with fresh apple, orange peel, and citrus odours, respectively, while aromatic aldehydes include benzaldehyde, with cinnamon and almond odours. Furthermore, notorious terpenoid aldehydes comprise safranal and citral, which give saffron and lemon aromas, respectively [2]. Several aldehydes are common and of potential concern in indoor residential and occupational environments; they are precursors of particulate matter and ozone formation in outdoor air [3]. Because of their reactivity, they can interact with electron-rich biological macromolecules, producing adverse effects for health, such as allergenic reactions, genotoxicity, and carcinogenicity [4]. Thus, due to the numerous critical issues that arise for aldehydes, several methods have been reported in the last years for their detection, especially for the highly volatile aliphatic aldehydes, such as formaldehyde, acetaldehyde, and furfural [5,6]. On the other hand, many aldehydes present in different types of essential oils have been demonstrated to possess interesting biological activities, for instance, reducing the antimicrobial resistance (AMR) to act as antimicrobial agents, balancing menstrual cycles, being efficient as an immune system booster [7], and possessing tonic, antipyretic, spasmolytic, calming, vasodilator, and antiviral activities [8]. An overview of aldehyde-forming reactions in biological systems and beyond has been recently reported [9]. Moreover straight-chain aliphatic aldehydes have often been found in the breath of patients suffering from lung diseases, asthma, and chronic obstructive pulmonary disease (COPD), suggesting their use as biomarkers for these diseases [10–12]. Nevertheless, notwithstanding the important role of aldehyde dehydrogenases (ALDHs) in the detoxification of aldehydes [13], studies regarding the toxicity of these compounds and restrictions of aldehydes in cosmetics are increasing. Recently, 2-(4-*tert*-butylbenzyl)propionaldehyde (BMHCA), which has been recognized as a potential threat for humans, is actually submitted to restrictions in Europe due to its potential toxicity. Moreover, it must be considered that often aldehydes are present in topically applied medical devices, in the form of gels and creams, which can be applied to damaged skin. However, unlike cosmetics, these products are not subject to restrictions when used in medical devices [14]. In this review, we summarize the most common VOCs, specifically aldehydes, both aliphatic and aromatic, present in PPCPs and in foods, focusing on the recent studies about their potential toxicity and threat for humans (Figure 1). Moreover, given that each aldehyde often has multiple names, they have been catalogued in paragraphs and tables, reporting all the names attributed to each single compound.

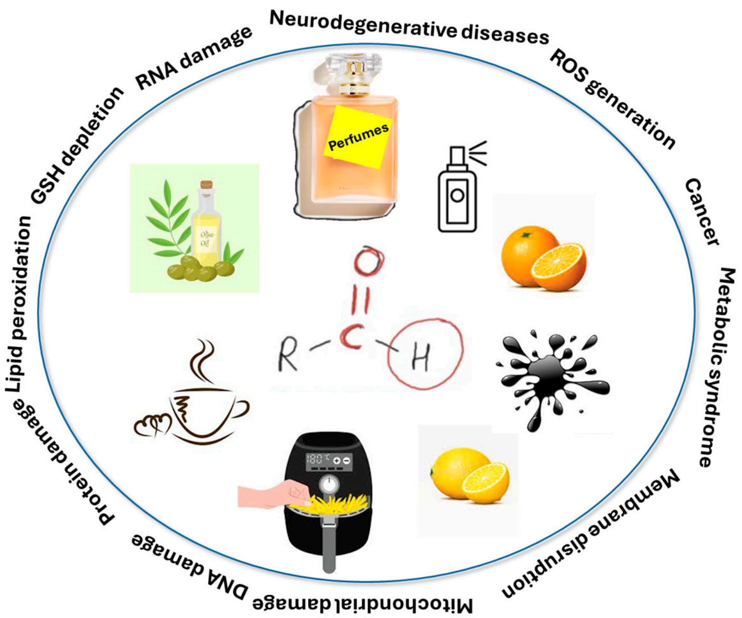


Figure 1. Sources and toxicity of aldehydes.

2. Volatile Organic Compounds (VOCs)

Flavours and fragrances belong to the VOCs, which are categorized by the World Health Organization (WHO) as compounds with a boiling point of 50–250 °C at atmospheric pressure [15,16]; thus, they can be found indoors in the gaseous phase. They can be found in personal care products (PCPs), also defined as personal care and household products (PCHPs), which include perfumes, creams, lotions, detergents, and so on, as well as in food and in pharmaceuticals, to ameliorate or modify their odour and/or taste [17]. Electrophysiological studies showed that diverse fragrances affect brain activities and cognitive functions, with changes in the electroencephalogram [18]. The number of flavouring compounds utilized in daily products is very large, just considering that the list of Scientific Committee on Cosmetic and Non-Food Products (SCCNFP) contains 2750 entries as perfume and aromatic raw materials (SCCNFP, 2000) [19,20]. In order to establish the fragrances that may be safely used in foodstuffs, the European Food Safety Authority (EFSA) reported a list of compounds for which additional toxicity data have to be provided on the Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF) Panel [21]. VOCs include acids, alcohols, esters, and aldehydes, and they may be natural, such as those present in virgin olive oil, coffee, fruit, rice, and plants [22–25], or may derive from anthropogenic sources [26], including solvents, printing ink [27], PCPs, solvents, coating, pesticides [28–30], and deodorizers [31]. Domestic cooking is also an important source of VOCs [32]. Among the different categories of compounds found in indoor environments, VOCs can frequently reach higher concentrations compared to the corresponding outdoor values. Long-term exposure to VOCs may impact human health with negative cutaneous, respiratory, and systemic effects (e.g., headache, asthma attacks, breathing difficulties, and cardiovascular and neurological issues) and cause distress in workplaces; they may increase the risk of lung cancer, sick building syndrome, and other building-related illness [33–35]. The main point is that these "reactive" anthropogenic VOCs may produce secondary organic aerosols via photochemical reactions, leading to atmospheric pollution and adverse side effects in sensitive populations [36–38]. Additionally, several VOC degradation technologic procedures have been described [39].

3. Aldehydes

Aldehydes are carbonyl compounds found in nature with high reactivity, undergoing common reactions such as oxidation, reduction, and condensation [40–42]. Aldehydes are widely distributed indoors and outdoors, deriving from industrial, restaurant, and automotive waste, and are believed to be an important cause contributing to smog in the air. Some examples of famous perfumes that contain aldehydes are Chanel N°. 5, Lancôme Climat, Givenchy L'interdit, and D&G Sicily. It was Chanel N° 5 that popularized the usage of aldehydes in perfumes [43,44]. Aldehydes may also be found in rainwater and surface water, because of their leaching from the atmosphere and their high water solubility. Furthermore, the microbial or photochemical degradation of organic chemicals, as well as sterilization with chlorination and ozonation of drinking water, leads to the formation of aldehydes in surface waters. Finally, aldehydes may derive from high-temperature cooking or frying and also from cigarette smoke and/or other combustion activities [3,45–47]. Generally, the aldehyde content rises with an increase in temperature and/or time during the roasting process [48]. A recent study evidenced that air frying, which is becoming a popular method for domestic cooking, leads to the production of an amount of VOCs generally higher compared with conventional cooking with a pan [49]. Aldehydes may be found in wine and vegetal oil and may also represent by-products during the spoilage, maturation, or microbial fermentation of foods [50,51]. The "volatolome", consisting of VOCs emanated from the human body, was reported in 2014 for the first time [52]. Aldehydes have demonstrated various biological activities, such as antimicrobial, both as free compounds or complexed with metals [53], and this is useful in extending the shelf life of vegetables and fruit [54]. Moreover, the antioxidant activity of aldehyde Schiff bases [55,56] and their use in the catalysis of α-branched aldehydes have also been reported [57,58]. However, human exposure to aldehydes from food or from the environment can lead to some adverse health effects, both acute and chronic. Since the 1960s, formaldehyde, acrolein, crotonaldehyde, acetaldehyde, *i*-butanal, and *n*-butanal have been reported to exhibit toxicity [59]. The potential high toxicity of aldehydes is related to their high reactivity with biological molecules, which may lead to the disruption of biological activities, thus causing various disorders and diseases [60], such as allergies, hepatotoxicity, pulmonary toxicity, embryo toxicity, diabetes, hypertension, cerebral ischemia, cancer, neurodegenerative diseases, and other ageing-associated diseases [61,62]. Since inhalation is an important route of aldehyde exposure, the lung and heart are two of the major targets of aldehyde toxicity [63,64]. Recent studies have addressed the synthesis of aldehydes for flavours and the fragrance industry, focusing on new investigations to encourage the sustainable development of biotechnological solutions via the biocatalytic oxidation of alcohols and using photocatalytic strategies for the installation of the formyl group, in order to obtain so-called 'bio-aldehydes' [65–68]. Moreover, engineering microbial biosynthesis methods for the preparation of these compounds have been described [69].

4. Aliphatic Aldehydes

Aliphatic aldehydes are degradation products formed during the heat-induced oxidation of fatty acids, especially unsaturated fatty acids. They have intrinsic flavours and include saturated aldehydes, such as hexanal, heptanal, and decanal; monounsaturated aldehydes, such as hexenal, heptenal, and decenal; and three polyunsaturated aldehydes (2,4-hexadienal, 2,4-heptadienal, and 2,4-decadienal) [70]. Formaldehyde and acetaldehyde provide a key benchmark of the fuel ignition phenomena [71]. Several aliphatic aldehydes belonging to VOCs, such as acetaldehyde, butanal, 3-methylbutanal, pentanal, hexanal, octanal, nonanal, and decanal, have been identified by Head Space-Gas Chromatography/Mass Spectrometry (HS-GC/MS) in the PET bottles used for the packaging of six Italian brands of mineral water. Acetaldehyde, octanal, nonanal, and decanal were the most abundant compounds identified in the packaging and in the contained mineral water. These aldehydes are likely derived from epoxidized soybean oil or erucamide used as additives and are probably loaded during the blow-moulding processes used for PET bottle manufacturing [72]. A recent study conducted on chicken meat to identify the substances responsible for the characteristic aroma revealed that hexanal, (*E*)-2-nonenal, heptanal, and (*E*,*E*)-2,4-decadienal were breed-specific aroma compounds present in native Chinese chickens but not in the meat of white-feathered broilers [73]. The emissions of aliphatic aldehydes, such as formaldehyde, acetaldehyde, and acrolein as gas-phase air toxics produced by gasoline and diesel vehicles, are tracked by the EPA and California Air Resources Board (CARB) for monitoring air quality [74]. Some methods for their detection have been reported [75–77]. In addition, ozone reactions with carpet may lead to higher concentrations of aliphatic aldehydes, such as formaldehyde, acetaldehyde, and aldehydes with 5–10 carbons, leading to secondary emissions [31]. Formaldehyde (Group 1), acrolein (Group 2A), acetaldehyde, and crotonaldehyde (Group 2B) have been identified in tobacco smoke and are classified by the IARC as carcinogens. The formation of these compounds is mainly due to tobacco combustion and pyrolysis, since these compounds are poorly detected in unburnt tobacco [78]. In order to update the safety assessment process conducted by the Research Institute for Fragrance Materials, Inc. (RIFM), revised criteria were designed and published [79]. Aldehydes with 8–18 carbon atoms are most commonly used in formulating modern perfumes [44]. The implementation of REACH (the European Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals) added new data for chemicals including fragrance materials such as aldehydes [80]. The most common aliphatic aldehydes are summarized in Table 1.

Table 1. Structure of the most common aliphatic aldehydes.

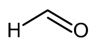
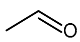
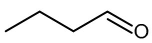
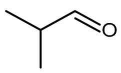
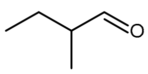
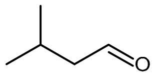
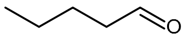
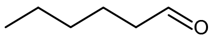
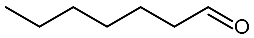
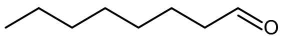
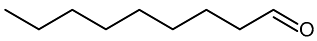
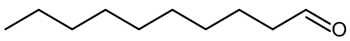
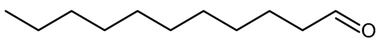
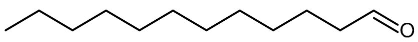
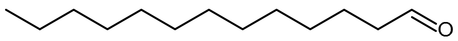
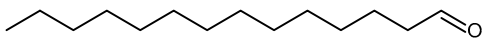
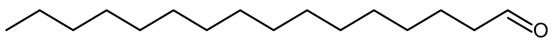
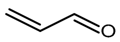
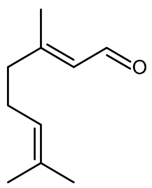
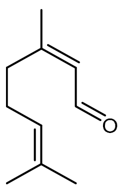
Structure	Formula	CAS Number	Name
	HCOH CH_2O	[50-00-0]	Formaldehyde (or methanal)
	C_2H_3OH C_2H_4O	[75-07-0]	Acetaldehyde (or ethanal)
	C_4H_7OH C_4H_8O	[123-72-8]	*n*-Butanal (or *n*-butyraldehyde)
	C_4H_7OH C_4H_8O	[78-84-2]	*i*-Butanal or *i*-butyraldehyde or 2-methylpropanal
	C_5H_9OH $C_5H_{10}O$	[96-17-3]	2-Methylbutanal

Table 1. *Cont.*

Structure	Formula	CAS Number	Name
	C_5H_9OH $C_5H_{10}O$	[590-86-3]	3-Methylbutanal or isovaleraldehyde
	C_5H_9OH $C_5H_{10}O$	[110-62-3]	Pentanal or valeraldehyde
	$C_6H_{11}OH$ $C_6H_{12}O$	[66-25-1]	Hexanal or caproaldehyde or caproic aldehyde or capraldehyde or capronaldehyde
	$C_7H_{13}OH$ $C_7H_{14}O$	[111-71-7]	Heptanal (or enanthaldehyde)
	$C_8H_{15}OH$ $C_8H_{16}O$	[124-13-0]	Octanal (or caprylaldehyde)
	$C_9H_{17}OH$ $C_9H_{18}O$	[124-19-6]	Nonanal (or pelargonaldehyde)
	$C_{10}H_{19}OH$ $C_{10}H_{20}O$	[112-31-2]	Decanal (or caprinaldehyde)
	$C_{11}H_{21}OH$ $C_{11}H_{22}O$	[112-44-7]	Undecanal
	$C_{12}H_{21}OH$ $C_{12}H_{22}O$	[112-54-9]	Dodecanal (or lauraldehyde or lauric aldehyde)
	$C_{13}H_{23}OH$ $C_{13}H_{24}O$	[10486-19-8]	Tridecanal
	$C_{14}H_{25}OH$ $C_{14}H_{26}O$	[124-25-4]	Tetradecanal (or myristyl aldehyde)
	$C_{16}H_{29}OH$ $C_{16}H_{30}O$	[629-80-1]	Hexadecanal
	C_3H_2OH C_3H_3O	[107-02-8]	Acrolein
	$C_{10}H_{15}OH$ $C_{10}H_{16}O$	[141-27-5]	Geranial or *Z*-citral or *cis*-citral or citral α or citral A
	$C_{10}H_{15}OH$ $C_{10}H_{16}O$	[106-26-3]	Neral or *E*-citral or *trans*-citral or citral β or citral B

4.1. *Formaldehyde (Methanal)*

Formaldehyde (or methanal) is a colourless, flammable, pungent-smelling, and highly reactive chemical that is recognized as a xenobiotic air pollutant and is universally distributed to humans [81,82]. Liquid formaldehyde, called formalin, which is widely used in anatomy laboratories to preserve cadavers, is an aqueous solution of formaldehyde (37%), normally with the addition of about 15% methanol to prevent polymerization. As the simplest aldehyde, it is synthesized by the catalytic oxidation of methanol. It is one of the major pollutants in indoor environments and is toxic, allergenic, and potentially carcinogenic to the human body. It may derive from smoking, cooking, heating, wood-based furniture, paints and textiles, building materials, decoration materials, furniture finishings, household products, cosmetics, plastics, medicines, and chemical reactions between VOCs and ozone [83]. It may also derive from the residues of food including fruits, vegetables, and meat, and can be generated in living organisms [84]. Formaldehyde-fixed paraffin-embedded techniques are widely used for tissue preservation in hospitals, brain banks, and research laboratories, allowing neuropathological evaluations of the human post-mortem brain. However, the formaldehyde-fixed tissues have diverse crosslinks between macromolecules, and Schiff base formation between proteins and formaldehyde may be observed [85]. Short-term exposure to formaldehyde may cause many symptoms, such as burning sensations in the nose, eyes and throat; coughing; wheezing; nausea; and skin irritation, whereas long-term exposure can lead to the onset of cancer [86]. Indeed, formaldehyde was identified as a Class 1 human carcinogen by the World Health Organization (WHO) in 2004 [87] and by the International Agency for Research on Cancer (IARC) in 2006, because there was sufficient evidence for it being a human cancer-causing agent (carcinogen), based on the results of epidemiological studies assessing an association with nasopharyngeal cancer in humans and squamous cell carcinomas in the nasal passages of rats. The IARC concluded that there was "strong but not sufficient evidence for a causal association between leukaemia and occupational exposure to formaldehyde" [88,89]. In 2014, formaldehyde was classified as a 1B carcinogen and mutagen by the European Commission [90]. In addition to the well-established risk to human health from formaldehyde environmental exposure, recent reports indicate that endogenously produced formaldehyde also represents a significant threat [91]. The mutagenic activity of formaldehyde is attributed to the electrophilic carbon, which may rapidly attack electron-rich thiols, as well as amino groups, forming covalent bonds [92]. Effectively, research conducted in an anatomy laboratory showed that cancer risk assessment for employees exposed to formaldehyde was several thousand times higher than the limit recommended by the Environmental Protection Agency (EPA) (10^{-6}) [93]. Kang et al. (2021) [94] analysed the potential association between formaldehyde exposure and leukaemia by exploring biological networks basing on formaldehyde-related genes retrieved from public and commercial databases. The authors found that oxidative stress-mediated genetic changes induced by formaldehyde might disturb the haematopoietic system, possibly resulting in leukaemia [94]. Moreover, formaldehyde exposure may be related to arthritis [95]. A recent review summarizes the in vitro and in vivo studies assessing the toxicity of formaldehyde [96]; however, the toxicity aspects for this chemical are controversial, and the causal relationship remains unclear because of the limited evidence demonstrating the effects of formaldehyde on the bone marrow and other distal organs [97]. In contrast, some toxicological and modelling studies indicated that formaldehyde does not reach regions far away from the primary exposure site and should not be expected to induce cancer, or any other endpoints, in these tissues [98]. Stringent formaldehyde exposure guidelines exist for indoor air (WHO Indoor Air Quality-IAQ-regulation established an upper limit of 80–100 ppb [99,100], or 100 μg/m^3 [101] for exposure within a short period of 30 min), which can be even lower at the national level in France (e.g., France 8 ppb by 2023) [102]. The olfactory limit of human beings for formaldehyde (410 ppb) [103] is far higher than the safety standard, making it difficult to avoid the harm caused by formaldehyde through our own olfactory system. In this context, the use of several sensors for selective formaldehyde detection at ppb levels has been reported [104,105]. A systematic review on exposure and early effect biomarkers for the risk assessment of occupational exposure to formaldehyde has been recently reported [106].

4.2. Acetaldehyde (Ethanal)

Acetaldehyde (or ethanal) is a simple aldehyde widely found in nature and produced on a large scale in industry; it is abundant in automobile exhaust and human daily necessities, which leads to water and environmental pollution. It contributes to the odour and tactile nasal perception of red wine [107] and is also used as an intermediate in organic syntheses. Acetaldehyde is a side product of cell metabolism, as it can react with genomic DNA to induce cell poisoning, causing major damage to the human body [77]. The inhalation of exogenous acetaldehyde may cause bronchitis, upper respiratory disease, denaturation, and/or death of proteins. Moreover, acetaldehyde is involved in the pathological physiological processes related to alcohol addiction of aldehyde-metabolized organisms [108]. Acute exposure to acetaldehyde has irritating effects on the eyes, skin, and respiratory tract, whereas the symptoms of chronic acetaldehyde poisoning are comparable to those of alcoholism [109,110].

4.3. n-Butanal (n-Butyraldehyde) and 2-Methylpropanal (Iso-Butyraldehyde or Iso-Butanal)

Several studies have addressed *normal*-butanal (*n*-butanal or *n*-butyraldehyde) and *iso*-butanal (*i*-butanal or *i*-butyraldehyde or 2-methylpropanal) in interstellar chemistry by the astrophysical community, as they have been identified in several chondritic meteorites as targets for interstellar detection [111]. *N*-Butanal is used in perfumery, pharmaceuticals, rubber accelerators, agrochemicals, and textile auxiliaries and can be easily prepared through the hydroformylation of propene and dehydrogenation from naturally obtained *n*-butanol by the use of copper nanoparticles on a silica support [112].

4.4. 2-Methylbutanal and 3-Methylbutanal (or Isovaleraldehyde)

2-Methylbutanal has a cocoa and almond aroma, while 3-methylbutanal has a malt aroma. These compounds contribute to the deep-fried flavour in more than 50% of fried products [113], they may also derive from cooking microwave popcorn [114] and are present in black tea [115]. 3-Methylbutanal and other branched-chain aldehydes are common volatile compounds in several cheeses [116]. 3-Methylbutanal is produced by the action of the microbiota in cheese starters [117], but it is also present in Chinese fried food of youtiao [118]. 2-Methylbutanal and 3-methylbutanal, as well as 2-methylpropanal, are also produced during the manufacture of Raclette-type cheese [119].

4.5. Pentanal (Valeraldeheyde)

Pentanal (or valeraldehyde) has a pungent and fruity odour that gives the classical aroma to chicken broth [120]. It has demonstrated excellent inhibition activity against *Aspergillus flavus* on both potato dextrose agar (PDA) plates and red pepper powder, thus being suggested as a promising bio-preservative able to prevent *A. flavus* contamination of red pepper [121]. It can be formed during the oxidation of n-6 PUFAs [122] and may exhibit pulmonary toxicity, affect sensory organ development, induce apoptosis, and alter reproductive developmental processes [123]. It has been demonstrated that the emission profile of pentanal and hexanal depends on the frying temperature: with an increase in temperature, a rapid release of these compounds can be observed in the first minutes of frying, as demonstrated in a recent study during the deep-frying of tubers [124]. The monitoring of exhaled pentanal in the breath of ventilated patients has been suggested as a potential non-invasive biomarker for lipid peroxidation-inducing disease for the detection of lung injury [125].

4.6. Hexanal (Caproaldehyde, Caproic Aldehyde, Capraldehyde, Capronaldehyde)

Hexanal (or caproaldehyde or caproic aldehyde or capraldehyde or capronaldehyde) is a crucial component of the scent of mulberry [126]. It is a biomolecule derived from plants that is characterized by a fatty-green pungent odour and taste, and in low concentrations, it is reminiscent of unripe fruit. In particular, it has a grass, green, tallow, fat, leafy, vegetable, fruity, clean, woody aroma; indeed, it is a main component of the emissions from stored wood pellets and is often found in living environments, office furniture, and millwork [127]. It occurs in apple [128], grape [129], carrot, and strawberry [130] aromas, as well as in orange and lemon oil [131], and it is also present in non-psilocybin and psilocybin mushrooms [132,133]. Hexanal has a grass, green, flower odour, and it is used for fruit flavours and, when very diluted, in perfumery to obtain fruity notes. It has been demonstrated that it is able to inhibit phospholipase D and decrease the deterioration of membranes in fruits. Occupational exposure routes for hexanal consist of inhalation, dermal contact, and food intake. Hexanal preharvest applications, generally as sprays, and postharvest applications have been used to improve the shelf life and delay senescence of fruits and vegetables [134–137]. The vapour of hexanal is an easy and cheap strategy to extend the shelf life of fruit [138,139]. However, adverse effects on human health have been documented, including pulmonary toxic effects evidenced in rats. It may exhibit pulmonary toxicity and affect the G-protein coupled receptor protein signalling pathway and induce the acute inflammatory response [140]. The study by Corradi et al. [141] evidenced that the levels of hexanal detected in patients with COPD is higher than those of smoking and nonsmoking control subjects. The use of hexanal as a cancer biomarker has been suggested since high levels of this aldehyde were detected in the breath of patients with lung cancer [142,143]. Finally, it should be evidenced that, sometimes, there is confusion about the name of aldehydes, and hexanal and capraldehyde are considered different compounds [144,145].

4.7. Heptanal (Enanthaldehyde)

Heptanal (or enanthaldehyde) has a fat, citrus, fruity, waxy, and rancid aroma. It was identified as a main component of several essential oils from *Aristolochia delavayi*, *Bupleurum longiradiatum*, *Kundmannia anatolica*, *Kundmannia syriaca*, and extracts from cyanobacteria and green algae. In addition, it is the main chemical component of cereal volatiles of postharvest grains [146,147]. Furthermore, it was found in solvent extracts of *Serapias orientalis* subsp. *orientalis* plants in 10.4% concentration, along with pelargonaldehyde (7%) and hexanal (2.1%) [148]. Heptanal has been recently suggested as a fast and non-invasive way to monitor the spread of COVID-19 [149], being identified as a key biomarker that was significantly elevated in the exhaled breath of SARS-CoV-2 patients [150]. In addition, the use of potential biomarkers containing hexanal and heptanal has been described for lung cancer [151], also in the saliva of patients [152]. Recently, the activity of heptanal as an antifungal against *A. flavus* was reported. The safety of heptanal was authorized by the Flavor Extract Manufacturers' Association [153].

4.8. Octanal (Caprylaldehyde)

Octanal is widespread distributed in the environment and represents an indoor air pollutant. Octanal has fat, soap, lemon, and green aromas possessing an odour threshold of only 0.01 mg/L. It occurs in several citrus oils, e.g., orange oil. It is a colourless liquid with a pungent odour (citrus, orange) and, on dilution, gives a citrus-like aroma. Octanal is used in low concentrations in perfumery, in eau de cologne, and in artificial citrus oils [154]. It is a bioactive component of *Houttuynia cordata*, which is studied for its antioxidant, anti-inflammatory, and antiviral properties against HIV and HSV, by blocking viral binding and the penetration of the viruses [155]. In addition, octanal was found to exert fungicidal activity against *Geotrichum citri-aurantii* in vitro, indicating effectiveness in controlling citrus postharvest pathogens [156]. Octanal has been demonstrated to be efficient in controlling green mould caused by *Penicillium digitatum*, thanks to a defence response mechanism; thus, it was suggested as an effective strategy for the control of postharvest green mould by triggering the defence response in citrus fruit [157]. It has been suggested that inflammation may contribute to octanal-induced lung damage, as octanal exposure is able to modulate the expression of several chemokines and inflammatory cytokines and enhances the levels of interleukin 6 (IL-6) and IL-8 release, which are involved in the development of lung injury [158].

4.9. Nonanal (Pelargonaldehyde)

Nonanal (or pelargonaldehyde) has a grassy, green, fat, citrus, floral, rose-like, waxy and fruity, pungent odour with a threshold of just 0.02 mg/L [159,160]. It is a clear brown liquid that is insoluble in water [44], and when employed at high levels, it is a significant part of citrus and rose notes. It occurs in citrus and rose oils and is used in floral compositions, especially those with rose characteristics. It has been reported as the key flavour substance, contributing to the intense grass-like aroma note, and the oily aroma of chicken soup [120,161,162].

4.10. Decanal (Caprinaldehyde)

Decanal (or caprinaldehyde) has a sweet, aldehydic, waxy, orange peel, citrus, floral aroma and is an ingredient of several essential oils (e.g., neroli oil). It is a colourless liquid with a strong odour, reminiscent of orange peel, which upon dilution, changes to a fresh citrus odour. Decanal is used in low concentrations in blossom fragrances (particularly for creating citrus nuances) and in the production of artificial citrus oils [44,163].

4.11. Undecanal

The 11-carbon undecanal is a unique compound that conveys a bitter and fresh effect in cologne formulas [44]. It is present in citrus oils. It is a colourless liquid with a flowery-waxy odour, which gives the sensation of freshness. Undecanal is defined as the prototype of the perfumery aldehydes and is broadly used in perfume compositions to give an aldehydic note.

4.12. Dodecanal (or Lauraldehyde or Lauric Aldehyde)

It is a colourless liquid with a waxy odour, present in many fragrances because of its intensity, and it has different qualities depending on the use [44]. At high dilutions, it is reminiscent of violets. Dodecanal occurs in various citrus oils and in small amounts in essential oils from several *Pinus* species. It is used in perfumery to confer fragrances with fatty-waxy notes. It is used to obtain citrus notes.

4.13. Tridecanal

It occurs in lemon oil and has been recognized as a volatile component of cucumber. It smells like grapefruit (citrusy smell) and can even enhance the smell of musk in a scent. It is a colourless liquid having a fatty-waxy, slightly citrus-like odour. Adding tridecanal to fragrance compositions imparts fresh nuances in the top note, as well as in the dry out [44]. Tridecanal is the aroma-characteristic compound of Hyuganatsu oil [164].

4.14. Tetradecanal (or Myristyl Aldehyde)

Tetradecanal or mirystyl aldehyde is an amalgam of peach aldehyde. It falls under the category of lactone (an organic compound that contains an ester) [165]. The odour profile is sweet and fruity (peachy), and even if used in small amounts, it is a potent compound [44,166]. This aldehyde is studied in orchids, as it plays a key role in the attraction of a wide variety of pollinator insects [167].

4.15. Hexadecanal

Hexadecanal is quite reminiscent of sweet candy and is also called strawberry aldehyde. Along with a strong fruity tone, this compound has a secondary hint of floral honey, making it very good for floral formulations [44]. Hexadecanal is a human body volatile that functions as a mammalian-wide social chemosignal that affects human aggression; thus, it has been suggested as a human signalling pheromone. It has been evidenced that sniffing hexadecanal blocks aggression in men and triggers aggression in women [168].

4.16. Acrolein (or Propenal)

Acrolein is a highly reactive unsaturated aliphatic aldehyde ubiquitously found as a common dietary and environmental pollutant, which seriously threatens human health and life. Acrolein is present in all kinds of foods, and dietary intake is one of the major routes of human exposure to this compound [169], but it can also be generated endogenously. Acrolein formed by lipid oxidation in a fried system with less sugar can form acrylamide and is classified as Group 2A by the International Agency for Research on Cancer [170] by the amino dehydroxylation reaction in the presence of ammonia [171,172]. Given its high reactivity, cytotoxicity, and genotoxicity, exposure to acrolein has been related to several diseases, including atherosclerosis, hepatic ischemia, diabetes mellitus, stroke, neurodegenerative diseases such as Parkinson's and Alzheimer's disease, multiple sclerosis, asthma, acute lung injury, COPD, and even lung diseases and respiratory cancers [173–176]. At the cellular level, acrolein induces diverse harmful effects, such as protein adduction and oxidative damages [177]. Thus, the use of acrolein scavengers in food is being investigated to improve patient symptoms in neurodegenerative diseases in the long term [178]. Traditional tobacco smokers and e-cigarette users undergo the harmful effects of acrolein [179], and high concentrations of acrolein were found in mainstream and side-stream tobacco smoke as well [180].

4.17. Citral

Citral (3,7-dimethyl-2,6-octadienal) is a mixture of geranial and neral (two acyclic monoterpene aldehydes that are geometric isomers) and is considered an important raw material in the fragrance, pharmaceutical, food, and cosmetic industries. Geranial is the *trans*-citral and has a strong lemony odour, while neral has a sweet odour. This monoterpene has a cucumber, orris, fat, and green aroma and naturally occurs in herbs, plants, and citrus fruits [181]. It is a well-known biologically active compound present in various essential oils [182] and possesses antimicrobial [183], insecticidal [184], expectorant, appetite-stimulating, and spasmolytic properties, while also behaving as a weak diuretic and anti-inflammatory agent [156,185]. Recently, the anticancer potential of this natural product has been described, where the *trans*-isomer, geranial, is more potent than the *cis*-isomer, neral, both in vitro and in vivo [186]. However, there is confusion about the isomerism of these compounds. Zheng et al. (2022) identified neral as the *cis*-isomer of citral and demonstrated that geranial is more potent than neral against *T. rubrum*, and both inhibit ergosterol biosynthesis by affecting ERG6 [187]. Moreover, recent studies also report the biological activity of citral as antimicrobial without distinction between the activity of the two isomers [188]. Given the importance of isomerism in the activity of drugs, studies on this compound should preferably address the single isomers.

4.18. Other Aliphatic Aldehydes

Other aldehydes are used in fragrances, even though they are less studied. They also belong to the Cramer Classification. The Cramer decision tree [189] is used for categorizing non-carcinogenic chemicals in order to determine their Threshold of Toxicological Concern (TTC) level [190]. Specifically, these aldehydes include 4-tricyclodecylidene butanal (Class III, High) [191], β,4-dimethylcyclohex-3-ene-1-propan-1-al (Class I, Low) [192], 1-methyl-4-(4-methyl-3-pentenyl)cyclohex-3-ene-1-carbaldehyde (Class I, Low) [193], and α,α,6,6-tetramethylbicyclo [3.1.1]hept-2-ene-2-propionaldehyde (Class II) [194].

5. Aromatic Aldehydes

Aromatic aldehydes are largely used in cosmetics due to their fragrance, are essential in the aroma of Huangjiu, and play a role in the almond and sweet aromas [195]. Lilial, Bourgeonal, Nympheal, and Cyclamen aldehydes are some of the aromatic aldehydes present in perfumes and represent the so-called "Lily-of-the-valley fragrances" or "Muguet aldehydes" [196–198]. Several aromatic aldehydes have shown antibacterial and antibiofilm activity, and recently, nanogels synthesized by crosslinking kiwifruit-derived DNA's primary amine and aromatic aldehydes, including cuminaldehyde, *p*-anisaldehyde, and vanillin, have demonstrated higher antibacterial effects in successfully protecting *Caenorhabditis elegans* from *Pseudomonas aeruginosa*-induced lethality [199]. However, the limit of these compounds is linked to their potential toxicity. 2-(4-*tert*-Butylbenzyl)propionaldehyde (BMHCA) is actually under restriction in Europe due to its potential toxicity, as described in detail below. Structurally related fragrance aldehydes, such as bourgeonal, cyclamen aldehyde, PHCA, and Nympheal, also adversely affect sperm formation in rats [200]. These compounds are summarized in Table 2 and analysed below.

Table 2. Structure of the most common aromatic aldehydes.

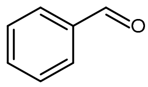
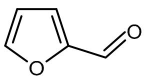
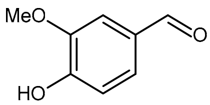
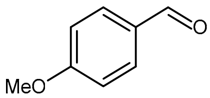
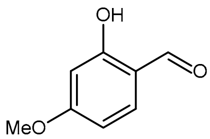
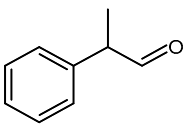
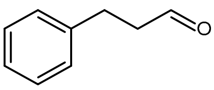
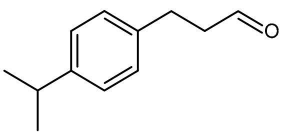
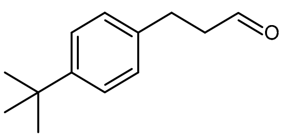
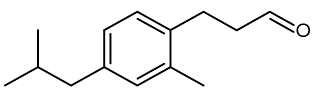
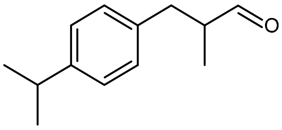
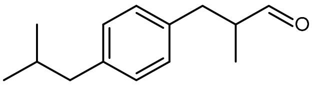
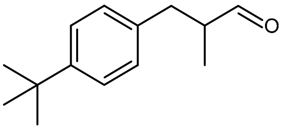
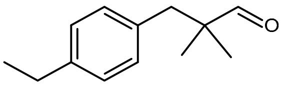
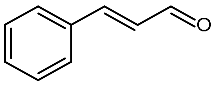
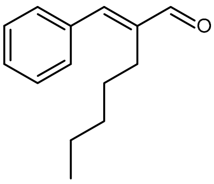
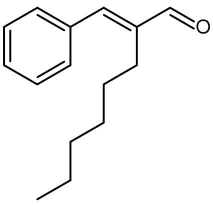
Structure	Name		Acronym and Trade Name
	Benzaldehyde	[588-68-1]	
	Furfural 2-Furaldehyde Furan-2-carboxaldehyde Pyromucic aldehyde	[98-01-1]	
	4-Hydroxy-3-methoxybenzaldehyde Vanillin	[121-33-5]	
	4-Methoxybenzaldehyde Anisaldehyde *para*-anisaldehyde, *p*-anisaldehyde	[123-11-5]	
	2-Hydroxy-4-methoxybenzaldehyde	[673-22-3]	HMB, HMBA
	2-Phenylpropanal	[93-53-8]	
	3-Phenylpropanal	[104-53-0]	
	3-(4-Isopropylphenyl)propanal 3-(*p*-Cumenyl)propionaldehyde	[7775-00-0]	PHCA
	3-(4-*tert*–Butylphenyl)propanal	[18127-01-0]	BHCA Bourgeonal Lilional Isolilial
	3-(4-Isobutyl-2-methylphenyl)propanal	[1637294-12-2]	Nympheal

Table 2. *Cont.*

Structure	Name		Acronym and Trade Name
	3-(4-Isopropylphenyl)-2-methylpropanal Cyclamen aldehyde Cyclamal 3-*p*-Cumenyl-2-methylpropionaldehyde	[103-95-7]	PMHCA CPA Floral
	3-(4-Isobutylphenyl)-2-methylpropanal *iso*-Butyl-α-methylhydrocinnamic aldehyde	[6658-48-6]	iBMHCA Silvial®
	2-(4-tert-Butylbenzyl)propionaldehyde. *p*-*t*-Butyl-α-methylhydrocinnamic aldehyde	[80-54-6]: (*RS*) [75166-30-2]: (*S*)-isomer [75166-31-3]: (*R*)-isomer	BMHCA Lilial, Lismeral
	3-(4-Ethylphenyl)-2,2-dimethylpropanal Ethyl-α-dimethylhydrocnamicaldehyde	[67634-15-5]	Floralozone Florone
	Cinnamaldehyde, Cinnamic aldehyde Cinnamal	[14371-10-9]: *trans* [57194-69-1]: *cis*	
	Amyl cinnamal, Amyl cinnamaldehyde Jasminaldehyde	[122-40-7]	
	α-Hexylcinnamaldehyde	[101-86-0]	HCA

5.1. *Benzaldehyde*

Benzaldehyde is the simplest member of the family of aromatic aldehydes. It is a clear, colourless to slightly yellowish oil, with an odour of bitter almonds and a burning aromatic taste. This characteristic odour is related to the trace amounts of free benzaldehyde, formed by hydrolysis of the glycoside amygdalin. Due to the reactive aldehyde hydrogen, the carbonyl group, and the benzene ring present in its structure, benzaldehyde is a versatile intermediate [201]. It is used in the chemical industry as a solvent and plasticizer and is considered a toxic pollutant if inhaled, causing nose and throat irritation; thus, a sensitive and selective detection method of benzaldehyde is often required [202]. Benzaldehyde is used in cosmetics as a denaturant, flavouring agent, and fragrance [203]. Benzaldehyde is considered a GRAS (Generally Regarded as Safe) food additive in the United States and a flavouring substance in the European Union [204–206]. Benzaldehyde is absorbed through the skin and lungs and is then distributed to organs, but it does not accumulate in any specific tissue type. It is rapidly metabolized to benzoic acid, then conjugated with glucuronic acid or glycine, and excreted in the urine. The use pf benzaldehyde as an antimicrobial compound against bacteria and fungi has been widely demonstrated [206].

Its potent heat-sensitizing action has been suggested to improve the efficacy of sanitary measures against *A. flavus*-contaminated crop seeds [207]. Studies regarding its potential carcinogenicity are controversial. It was evaluated by the National Toxicology Program, which found evidence of carcinogenicity in mice but not in rats. However, some studies have suggested that benzaldehyde may have antitumor properties [208].

5.2. Furfural (2-Furaldehyde, Furan-2-Carboxaldehyde, Pyromucic Aldehyde, Pyromucic Aldehyde)

Furfural is a colourless, oily liquid with a pungent and aromatic odour that is produced or used in many industries such as petrochemicals, pharmaceuticals, oil refineries, food, and paper industries. It finds application in the manufacturing of more than 1600 chemical products, including rubber, synthetic resins, wetting agents, food flavouring agents, PCPs, and pesticides [209]. Furfural and its derivatives, especially 5-hydroxymethylfurfural, are also found in coffee, fruit, honey, vinegar, breakfast cereals, baked bread, milk, beverages, and fruit juices [210,211]. Furfural is considered a toxic compound with an LD_{50} of 65 mg/kg. Indeed, several methods for its removal from both aquatic and non-aquatic habitats have been proposed [212,213].

5.3. 4-Hydroxy-3-Methoxybenzaldehyde (Vanillin)

4-Hydroxy-3-methoxybenzaldehyde (or vanillin) is the main component of natural vanilla, which is one of the most widely used and important flavouring materials worldwide, possessing a rich, creamy, and distinctive vanilla smell. The source of vanilla is the bean, or pod, of the tropical Vanilla orchid, but it also occurs in trace amounts in other plants, such as tobacco [214]. Vanillin is the second most popular flavouring agent after saffron and has wide applications, e.g., as an additive in food and beverages (about 60%), as a masking agent in various pharmaceutical formulations (about 7%), and as a scent ingredient in the cosmetics sector (about 33%) [215]. However, plant-based vanillin can no longer meet the annual global demand for bio-vanillin; thus, it is generally chemically prepared. Three types of vanillin, namely, natural, biotechnological, and chemical/synthetic, are available on the market. Vanillin is used in food and non-food applications, in fragrances, and in pharmaceutical preparations. Only natural and nature-identical (biotechnologically produced from ferulic acid) vanillins are considered as food-grade additives by most food-safety control authorities globally [216]. New advances in the vanillin synthesis and biotransformation, obtained by using genetic/metabolic engineering of microbes, and sustainable methods for vanillin production from lignin on an industrial scale are carried out to overcome the toxicity of synthetic vanillin [217]. The use of natural deep eutectic solvent-based green extraction of vanillin has been suggested as an environmentally friendly approach for vanillin extraction, which leads to the production of a high-quality bioactive vanillin with lower environmental impact [218].

5.4. 4-Methoxybenzaldehyde (Anisaldehyde, para-Anisaldehyde, p-Anisaldehyde)

4-Methoxybenzaldehyde is derived from *Pimpinella anisum* L. and is used as an additive in the preparation of perfumes and in medicine for its antifungal property. It provides a sweet, floral, and strong almond odour of anise [219]. It is generally recognized as safe by the U.S. FDA and is often used as a food additive with antimicrobial and biofilm inhibition effects against *Vibrio parahaemolyticus* in salmon [220]. Recent studies have demonstrated that *p*-anisaldehyde can inhibit the growth of *P. aeruginosa* [221] and possesses antifungal activity against *Penicillium digitatum* and *P. italicum*, which are two postharvest pathogens in citrus, causing about 90% of the total loss of citrus fruit during storage and transportation [222], and *Aspergillus flavus* on peanut seeds [223], as well as *Candida* species [224]. Moreover, the combination with nistin has demonstrated activity against *Listeria monocytogenes* and *Staphylococcus aureus* [225,226]. However, 4-methoxybenzaldehyde may determine muscle atrophy, since it inhibits skeletal muscle myoblast differentiation by downregulating the expression of myogenic genes and upregulating muscle atrophy-associated ubiquitin ligases [227].

5.5. 2-Hydroxy-4-Methoxybenzaldehyde

2-Hydroxy-4-methoxybenzaldehyde (also called HMB or HMBA) [228,229] is a vanillin isomer flavour metabolite obtained from the root of medicinal plants [230], specifically *Hemidesmus indicus*, popularly known as '*Anantmul*' [231], *Decalepis salicifolia* [232], *Mondia whytei* [233], and *Decalepis hamiltonii* [234]. Its antibacterial activity against *Staphylococcus aureus* has been described, and the mechanism has recently been investigated [235]. Moreover, it exerts antifungal activity against *Aspergillus flavus* [236] and against *Fusarium graminearum* on wheat grains [237]. Recently, its involvement as an efflux pump inhibitor of *Proteus mirabilis* has been suggested [238]. Moreover, it appears to act through Excess Toll-like receptor 2 (TLR2) inhibition, followed by the modulation of agonist-induced cell migration, invasion, and angiogenesis, which can be useful in rheumatoid arthritis patients [239]. In accordance with Regulation (EC) No 1331/2008, it belongs to chemical group 23 (Commission Regulation (EC) No 1565/2000). Exposure to this substance does not raise safety concerns [228].

5.6. Phenylpropanals—Floral Aromatic Aldehydes

5.6.1. 2-Phenylpropanal and 3-Phenylpropanal

2-Phenylpropanal (hydratropaldehyde) is an isomer of phenylpropanal and has a fresh, green leafy-floral, tart, hyacinth odour [240]. This compound, along with its derivatives is used in chemistry [241]. 3-Phenylpropanal has the simplest structure of this family, with a green, aldehydic, floral, and melon odour [242], among molecules having different substituents and in various positions of the aromatic ring and/or on the side chain. It is used in chemical reactions [243–245].

5.6.2. 3-(4-Isopropylphenyl)propanal (PHCA) or 3-(*p*-Cumenyl)propionaldehyde

3-(4-Isopropylphenyl)propanal (PHCA) or 3-(*p*-cumenyl)propionaldehyde (Cyclemax^{TM}) has a fresh, floral, muguet odour, with a fruity melon nuance [200,240]. It is less studied and mentioned than the others [246]; however, studies on its potential toxicity were inconclusive, as detailed in the Notified classification and labelling according to the CLP (Classification, Labeling, and Packaging) criteria reported by the ECHA for this substance [247].

5.6.3. 3-(4-tert-Butylphenyl)propanal (BHCA, Bourgeonal, Lilional, Isolilial)

3-(4-*tert*-Butylphenyl)propanal (BHCA, Bourgeonal®, Lilional®, Isolilial), having a floral, green, muguet, fresh, powerful odour and a diffusive fresh floral muguet, with a watery green character, can be found in fragrances such as "Alien" (Thierry Mugler) [198]. This aldehyde is manufactured and/or imported to the European Economic Area (EEA) at 10–100 tonnes per annum. It is used by consumers and professional workers in a vast range of products but may be detrimental to organs through prolonged or repeated exposure, with long-lasting effects, causing skin irritation and allergic skin reaction (ECHA) [248]. It may also adversely affect sperm formation in rats [200] and has been suggested to have the same activity in birds [249].

5.6.4. 3-(4-Isobutyl-2-Methylphenyl)propanal (Nympheal®)

3-(4-Isobutyl-2-methylphenyl)propanal (Nympheal®) was discovered by Andreas Goeke, Philip Kraft, Heike Laue, and coworkers at Givaudan in the search for a non-toxic Lilial® replacement in 2014 [250]. Among several designed compounds, Nympheal emerged as unique, not only in terms of odour threshold and olfactory qualities, but it also lacked adverse effects in a 28-day male rat reproductive toxicity study. It was hypothesized that the metabolic pathway leading to benzoic acid is disrupted by steric means of the adjacent methyl group [200,251]. Nympheal has a floral and aldehydic aroma. The name took inspiration from the painting series "Les Nimpheas" by Claude Monet [197].

5.6.5. 3-(4-Isopropylphenyl)-2-Methylpropanal (Cyclamen Aldehyde, PMHCA) or 3-p-Cumenyl-2-Methylpropionaldehyde (CPA)

Cyclamen aldehyde (3-(4-isopropylphenyl)-2-methylpropanal, PMHCA, cyclamal, 3-*p*-cumenyl-2-methylpropionaldehyde, Floral) is a commonly used fragrance material for its fresh flower smell (cyclamen, lilac, and violet) [252,253]. Among the synthetic molecules employed in perfumery, it is one of the most employed to recreate the muguet sensation. The presence of a stereogenic centre leads to the existence of two enantiomers, (*R*)- and (*S*)-cyclamen aldehyde [254]. In vivo studies in rats have demonstrated side effects on sperm maturation, likely related to the metabolite *p*-isopropyl-benzoic acid (*p*-iPBA). The in vitro accumulation of *p*-iPBA conjugated to coenzyme A (CoA) represents a metabolic sign related to reproductive toxicity in male rats. However, recent studies in rat, rabbits and human suspended hepatocytes demonstrated differences among the diverse species, where *p*-iPBA was detected only in rat hepatocytes. In plated rat hepatocytes, *p*-iPBA was conjugated to CoA, and the conjugate *p*-iPBA-CoA accumulated to stable levels over 22 h. *p*-iPBA-CoA was formed in vivo in the liver and testes of rats exposed to cyclamen aldehyde, whereas in plated rabbit and human hepatocytes, *p*-iPBA-CoA did not accumulate; thus, it was concluded that rabbits and humans are unlikely to be vulnerable to hepatic and testicular toxicity caused by *p*-iPBA [255].

5.6.6. 3-(4-Isobutylphenyl)-2-Methylpropanal (iBMHCA, Silvial®)

Silvial® is a trademark registered by Givaudan; the odour of Silvial is described as a "powerful, vibrant muguet ingredient with a slight citrus undertone and a fresh, aldehydic touch" [256]. The IFF (International Flavors and Fragrances) reports that canthoxal is reminiscent of "licorice, basil, fennel, anise note with a slight fruity, watery modification" [257]. The enantioselective synthesis of the (+)- and (−)-Silvial enantiomers has been recently described, and the olfactory activity of the single enantiomers has been evaluated [258]. The authors found that the (+)-enantiomer has a strong, floral, fatty, creamy, green, aldehydic, typically lily of the valley odour, whereas the (–)-isomer has a weak, floral, muguet, lilial-like odour. The odour detection threshold of the (+)-enantiomer is about five times lower than the one of the isomer.

5.6.7. 2-(4-tert-Butylbenzyl)propionaldehyde (BMHCA, Lilial, Lysmeral)

This synthetic compound [2-(4-*tert*-butylbenzyl)propionaldehyde] is generally known by its acronym, BMHCA, and its INCI (International Nomenclature Cosmetic Ingredient) name butylphenyl methylpropional. Several names are used to indicate this compound, as follows: BMHCA; benzenepropanal, 4-(1,1-dimethylethyl)-α-methyl-; *p*-*t*-butyl-α-methylhydrocinnamaldehyde; *p*-BMHCA; *p*-*t*-butyl-α-methylhydrocinnamic aldehyde; α-methyl-β-(*p*-*t*-butylphenyl)propionaldehyde; *p*-*t*-bucinal; *para*-*tert*-bucinal; 2-(4-*tert*-butylbenzyl) propionaldehyde; butylphenyl methylpropional; 3-(4-*tert*-butylphenyl)-2-methylpropanal; 4-(1,1-dimethylethyl)-α-methylbenzene propanal; and *p*-*t*-butyl-α-methylhydrocinnamic aldehyde. It is also known by its trade names, including Lilial®; Lysmeral®Extra; Lilyal; and Lilestralis®. Other names can be found in the scientific literature: Lilyal; pt-bucinal; and BPMP [259]. It is a synthetically produced aliphatic-aromatic aldehyde reminiscent of the smell of lily of the valley. BMHCA is a high-tonnage perfumery ingredient found in cosmetic and non-cosmetic products: it is present in hair oils (about 3%), deodorant sprays, specific hair care products, body milk, creams, and perfumes for women at about 2% concentration. Obviously, the predominant exposure route is dermal, but lysmeral can also be inhaled to a smaller extent [260]. The first studies on the toxicity of this drug were performed in 1980 and 1982 by Roche for the photosensitizing of guinea pigs. In 1984, the first studies on the mutagenicity of this compound were performed using the Salmonella/mammalian microsome plate incorporation assays. In 1986, acute respiratory sensory irritation, photoallergenicity, and acute eye irritation were recorded in mice and guinea pigs. Then, in 1990, hypersensitivity in albino guinea pigs was also reported. All these studies were not published but were summarized in detail by Bernauer et al. [261].

In 2008, BMHCA was suspected as a carcinogenic, mutagenic, and reprotoxic agent in humans, based on work by BASF SE (Kamp) researchers in male rats, and then it was found to induce premature births and to be environmentally harmful to aquatic organisms. Because of the observed reproductive toxicity effects in male rats, BASF classified BMHCA as CMR 2 (i.e., suspected to have carcinogenic, mutagenic, or reprotoxic potential for humans) [262], and in 2021, BMHCA was listed in the Annex II (n. 1666) [263], the list of substances whose presence in cosmetics is prohibited [264,265]. Moreover, the European Chemicals Agency Risk Assessment Committee evaluated a classification proposal of Lilial to be considered as toxic to reproduction (Commission 2021/1902). Since 1 March 2022, the use of BMHCA in cosmetic products has been prohibited, due to the CMR 1B classification in Europe [266]; however, it was not banned in household cleaners and detergents [267,268]. Since then, every month, new lists of products (perfumes, shampoos, soaps, body creams, cleansing milks, and household hygiene products such as detergents) retired from the market and containing this compound appear on the web (last ones September [269] and October 2023 [270]), based on the database of the RAPEX (Rapid Alert System for Dangerous Non-Food Products) system. The latter represents an early warning system for safety management by the European Commission (EC) and has a dedicated public website, the "Safety Gate", which provides access to weekly updates of alerts submitted by national authorities participating in the system [271]. In the database of this system, information about dangerous cosmetic products sold in the EU market can be found [272]. However, it should be considered that Cosmetic Regulatory Frameworks differ all around the world [273]. The Food and Drug Administration (FDA) and Health Canada, similarly to the EU, publish some lists for the control of cosmetic ingredients, even though they are not as comprehensive as the EU ones. Canada has the Cosmetic Ingredient Hotlist [274], whereas the FDA has a list of a limited number of prohibited and restricted ingredients [275] and an additional Cosmetic Ingredient Review (CIR), which is an industry-funded panel of medical and researcher experts that review and evaluate the safety of many ingredients used in cosmetics [276,277]. In 2023, the European Chemical Agency (ECHA) classified BMHCA as a strong allergen (skin sensitizer), reproductive toxicant (carcinogenic, mutagenic, or toxic to reproduction, CMR 1B classification), and suspected endocrine disruptor [278]. The ECHA reported that oral administration of BMHCA produced testicular and spermatotoxic effects in rats, including disturbed spermiogenesis and spermatogenesis in tubuli seminiferi, affected sperm parameters (counts, motility, and morphology), and led to a decreased reproductive performance [279]. The ability of BMHCA to act as an androgen receptor agonist and the estrogenic and androgenic activity of its metabolites have not been tested yet. However, the evaluation as an endocrine-disrupting chemical is under assessment by the ECHA [280].

The uptake of *p*-BMHCA results in the formation of the metabolite *para-tert*-butyl-benzoic acid (*p*-TBBA), which is excreted as the main metabolite in the urine of test animals [279] or humans [260]. *p-tert*-Butyl-benzoic acid (*t*BBA) is formed in vitro in rat hepatocytes, and it is suspected to be responsible for the toxic effects [200,281]; the *para* substitution is likely involved in the toxic activity. Indeed, the application of the *meta* substituted fragrance aldehyde 3-(3-*tert*-butylphenyl)-2-methylpropanal (*m*-BMHCA) did not result in testes and sperm toxicity [200,282]. In the ex vivo study by Hareng et al. (2023) [246], an experiment was carried out using a 3D cell culture with primary seminiferous tubules from juvenile Sprague Dawley rats (Bio-AlteR® system) in order to investigate the relation between p-BMHCA-induced testicular/sperm toxicity and CoA conjugation of p-TBBA as the main metabolite of p-BMHCA. In this study, the two position isomers (*para versus meta*) of TBBA were studied. The authors concluded that *p*-TBBA-CoA conjugates are formed at *p*-TBBA concentrations affecting the spermatogenic processes. Moreover, a difference between *p*-TBBA and *m*-TBBA in disrupting spermatogenesis and CoA conjugate formation was observed, which identifies systemic *p*-TBBA and intracellular *p*-TBBA-CoA conjugate formation as a crucial metabolic event for *p*-BMHCA-induced testicular toxicity. It should be noted that the first studies on the toxicity of *p*-TBBA date back to ancient times [283,284]. On the other hand, there are a number of contradictory publications presenting inconsistent research data. In a study on the risk assessment conducted by the French Agency for Food, Environmental and Occupational Health and Safety (ANSES) in diapers, it was demonstrated that BMHCA penetrates only to a limited extent [285].

The article by Bernauer et al. (2017) [261] reported that the "Scientific Committee on Consumer Safety (SCCS) indicated that genotoxicity potential of BMHCA cannot be excluded". In 2020, Api et al. [286] reported an in-depth study on this substance based on the RIFM Criteria Document. The authors found no genotoxicity for this substance and defined the Maximum Acceptable Concentrations in Finished Products (%). Moreover, the authors assessed that BMHCA is not PBT (Persistent, Bioaccumulative, and Toxic) as per the IFRA (International Fragrance Association) Environmental Standards, and its risk quotients, based on its current volume of use in Europe and North America, by PEC/PNEC (Predicted Environmental Concentration/Predicted No Effect Concentration) data, are less than 1. Furthermore, the mutagenic activity of BMHCA was evaluated in a bacterial reverse mutation assay conducted in compliance with GLP (Good Laboratory Practice) regulations and in accordance with OECD TG 471 on *Salmonella typhimurium* strains TA98, TA100, TA1535, and TA1537 and *Escherichia coli* strain WP2uvrA using the standard plate incorporation and preincubation methods. The authors concluded that the majority of data in bacteria provide no evidence for the mutagenic potential of BMHCA. Jablonská et al. (2023) [287] recently reported a set of in vitro assays, including resazurin, CHO/HPRT mutation, γH2AX biomarker-based genotoxicity, qPCR, and in vitro reporter luciferase assays for the oestrogen, androgen, NF-κB, and NRF2 signalling pathways. The authors demonstrated that neither lilial nor its metabolites showed a negative effect on cell viability, at a concentration up to 100 μM. It was also evidenced that BMHCA was not an oestrogen or androgen receptor agonist, nor could BMHCA metabolites bind oestrogen or androgen receptors. Lilial and its metabolites did not show any nephrotoxic effect on human renal tubular cells, as assessed by the mutagenic activity in CHO-K1 cells up to 100 μM. BMHCA is a chiral compound [288]: it may exist as two isomers, namely, (2*S*)-3-(4-*tert*-butylphenyl)-2-methyl propanal and (2*R*)-3-(4-*tert*-butylphenyl)-2-methylpropanal. The isolation of the pure enantiomers is very difficult because of the presence of an α-chiral aldehyde bearing an asymmetric secondary carbon atom next to the carbonyl moiety. The pure enantiomers may easily racemize after isolation via keto-enol tautomerism. Nevertheless, further studies on the two enantiomers should be carried out. Moreover, biological and social diversities associated with sex and age as well as their interdependencies must be taken into account in human biomonitoring studies, since differences in exposure to lysmeral and the formation of its metabolite have been demonstrated [289,290]. Recent studies showed that several BMHCA-like chemicals induced male reproductive toxicity in animals [200,291].

5.6.8. 3-(4-Ethylphenyl)-2,2-Dimethylpropanal (Floralozone, Florone)

3-(4-Ethylphenyl)-2,2-dimethylpropanal (Floralozone™, Florone®) has a powerful, clean, green odour, containing a fresh air note reminiscent of the ocean breeze. It forms a typical aquatic accord that can be found in fragrances such as "Cool Water Fem" (Davidoff), "L'Eau d'Eden" (Cacharel), and "Polo Sport Woman" (R. Lauren). Floralozone is a colourless liquid first discovered in Lagotis Gaertn and is now mainly synthesized industrially. The interest in this compound has recently grown owing to its various activities. It has shown to improve cognitive dysfunction in rats with vascular dementia [292] and to inhibit atherosclerosis [293], and it has been suggested as a new possible strategy to treat ischemic stroke [294].

5.7. Cinnamaldehyde and Derivatives

5.7.1. Cinnamaldehyde (Cinnamic Aldehyde, Cinnamal, 3-Phenylacrolein, 3-Phenylpropenal)

Cinnamaldehyde is the major bioactive component obtained from the internal bark of Cinnamon trees [295]. The scent and aroma of cinnamon likely act as cognitive stimuli, which may ameliorate impairments in memory, visual-motor capacity, and virtual memory due to the presence of cinnamaldehyde [296]. Several activities have been reported for cinnamaldehyde: it may prevent fasting-induced hyperphagia, lipid accumulation, and inflammation in high-fat diet-fed mice and has been suggested as a therapy for rats with allergic rhinitis, as it demonstrated vascular congestion and plasma cell, eosinophil, and inflammatory cell infiltration into the lamina propria in rat models [297,298]. In vitro studies also showed that adding cinnamaldehyde to a cell medium can reduce tau and amyloid β aggregation and increase cell viability [299]. It has also been shown that cinnamaldehyde may be a useful compound in the treatment of caries, as it acts as an antimicrobial against *S. mutans* biofilm at sub-MIC levels and modulates hydrophobicity, aggregation, virulence gene expression, acid production, and tolerance [300,301]. In addition, cinnamaldehyde's potential in the treatment and prevention of cancer has been recently underlined, as it regulates several signalling pathways that are effective against cancers [302]. Moreover, the potential use of cinnamaldehyde as a coadjuvant preventive treatment for COVID-19 disease has been recently suggested [303,304]. It showed anti-inflammatory activity and was able to reduce the SARS-CoV-2-induced cytokine storm by significantly reducing IL-1β release in an in vivo lung inflammatory model [303]. *Trans*-cinnamaldehyde has shown antimicrobial activity towards fungi, bacteria, and biofilms, as well as anti-mould, anti-diabetes, neuroprotective, and antioxidant activities [305–307]. It has even been suggested as a new candidate to curb bacterial resistance [308,309]. *Trans*-cinnamaldehyde is Generally Recognized as Safe (GRAS) by the U.S. FDA and the Flavour and Extract Manufacturer's Association (FEMA) and has been granted A status (i.e., may be used in foodstuffs) by the Council of Europe [310]; thus, it is considered a safe food and flavour additive. However, it presents low water solubility, and in vivo, it may decompose to cinnamic acid. Moreover, it often causes allergic reactions as a constituent of perfumes and cosmetics, leading to the limitation of its use by the International Fragrance Research Association (IFRA) to 0.05% [311]. Recent in vitro Ames tests assessed the mutagenicity of cinnamaldehyde [312]. However, Alves et al. (2023) [313] recently reported an in vivo study on a pharmaceutical formulation (orabase ointment) containing cinnamaldehyde for the treatment of oral fungal infection. The authors demonstrated that in *Galleria mellonella* larvae, cinnamaldehyde was not toxic up to the highest dose tested (20 mg/kg) and was not genotoxic up to a dose of 4 mg/kg in a mouse model. In a study in which the potency range of known allergens for the risk of inducing skin sensitization encompasses at least five orders of magnitude, cinnamaldehyde was categorized as a moderate sensitizer, with doses ranging between 500 and 2500 μg/cm^2 [314].

5.7.2. Amyl Cinnamal (Jasminaldehyde, Amyl Cinnamaldehyde)

Jasminaldehyde has a sweet, floral, oily, and waxy odour; it also has jasmine, honey, fruity, herbal undertones and some metallic, green, aldehydic character. It is present in perfumes and as a highly tenacious raw material commonly used in floral compositions for shampoos; soaps; detergents; in rinse-off, leave-on, and make-up products; deodorants; and room fresheners [315]. It is quite stable, but when heated, jasminaldehyde gets oilier and rancid in profile [316]. It has been recently studied for its effect on the fume suppression mechanism and road performance of styrene-butadiene-styrene asphalt, where amyl cinnamaldehyde-modified asphalt has been shown to be promising in fume prevention and emissions reduction [317].

5.7.3. α-Hexylcinnamaldehyde (HCA, Hexyl Cinnamal)

α-Hexylcinnamaldehyde (or hexyl cinnamal) is a broadly used fragrance chemical because its scent resembles jasmine, a typical floral scent, which makes it suitable to be used as a fragrance in PCPs (perfumes, shampoos, and creams) and household products and as a flavouring additive in food and the pharmaceutical industry. In the perfume and cosmetics industry, synthetic hexyl cinnamal is used, but it can be found naturally in chamomile oil [318]. This ingredient may cause an allergic skin reaction, and it is labelled by The European Chemicals Agency as a skin sensitizer [319]. Along with dodecanal and decanal, α-hexylcinnamaldehyde is one of the top five key compounds contained in *Jasminum grandiflorum* L. flowers [320]. It has been described as an endocrine-disrupting chemical included in synthetic detergents and air fresheners along with other compounds belonging to the same class [321].

6. Toxicity of Aldehydes and Mitigation of Their Toxic Effects in Humans

Toxicity from exposure to aldehydes has been widely described. The oxidative degradation of lipid membranes, also known as lipid peroxidation, generates over 200 types of aldehydes, many of which are highly reactive and toxic, including malondialdehyde, nonenal, 3,4-dihydroxyphenylacetaldehyde, 4-hydroxy-2-nonenal acrolein, and formaldehyde. The accumulation of these aldehydes has been related to Alzheimer's disease, Parkinson's disease, metabolic syndrome and alcohol intolerance [322–324]. At the molecular level, aldehydes damage DNA and can cross-link DNA and proteins, thus leading to other diseases, including cancer, Fanconi's anaemia, and Cockayne syndrome [325–327]. Moreover, an increased risk of cardiovascular disease was also attributed to the accumulation of aldehydes (secondary to alcohol consumption, ischaemia, or elevated oxidative stress) [328]. To mitigate the toxicity and pathogenesis related to aldehydes, the human body has several aldehyde-metabolizing systems such as aldehyde oxidases, cytochrome P450 enzymes [329], aldo-ketoreductases, alcohol dehydrogenases, short-chain dehydrogenases/reductases, and ALDHs [62]. These enzyme systems maintain a low level of aldehydes in the body by catalytically converting them into less-harmful and easily excreted products. ALDHs are able to detoxify a wide variety of endogenous and exogenous aldehydes to their corresponding carboxylic acids, thus helping to protect from oxidative stress and contributing to cellular and tissue homeostasis. The family of ALDHs contains 20 isozymes that are located in different subcellular compartments such as the cytosol, mitochondria, nucleus, and endoplasmic reticulum [62,330,331]. ALDHs also play a role in scavenging reactive oxygen species from aldehyde accumulation, thereby reducing oxidative stress in cells [332].

7. Methods for Removal of Aldehydes from Water and Air

Several methods have been described for the removal of aldehydes from aqueous solutions [333] The most common depuration solutions consist of steps of adsorption, oxidative [334,335], and biological processes, such as phytoremediation, i.e., a plant-based removal system [336]. In some cases, a combination of more than one method is required [337,338], especially when pollutants are particularly difficult to remove to the limits imposed by the law. Wang et al. (2020) [339] described the efficient removal of formaldehyde from water, with up to 99% removal efficiency, using a mesoporous calcium silicate hydrate. Salehi and Shafie (2020) [340] reported the dynamic adsorption of acetaldehyde from water on strong anionic resin of AMBERLITE IRA 402-OH after a pre-treatment with bisulfite obtaining an 86% pollutant removal. A solid surface including silica and polymer-linked systems are used as adsorbents to remove environmentally hazardous aldehydes from wastewater streams. Different aldehyde scavengers can be attached to the solid surface. Moreover, chitosan, a naturally occurring amine-rich polymer with diverse activities, can also be used for aldehyde removal [341].

The removal of anthropogenic pollutants such as aldehydes from the atmosphere consists of oxidation reactions, with the reaction of hydroxyl radicals being one of the most effective means [342]. Moreover, phytoremediation appears to be a low-cost, environmentally friendly solution for improving indoor air quality [343]. A vertical wetted-wall corona discharge reactor and a photocatalytic oxidation reactor were used for the removal of acetaldehyde in air [344,345]. Materials such as activated carbon, metal–organic frameworks, and mesoporous silica nanoparticles are also used for air quality remediation owing to their overall high surface area and accessibility of surface functionalization [346]. Wu et al. (2012) [347] described a collector design that placed cooking fumes in contact with a NaClO solution, reducing aldehyde concentrations up to 76% and emissions to 91%, which may represent a cost-effective measure for small food carts. In addition, the utilization of metal–organic frameworks for the adsorptive removal of an aliphatic aldehyde mixture in the gas phase was reported by Vikrant et al. (2020) [348]. Further, the removal of three aldehydes, specifically formaldehyde, acetaldehyde, and acrolein, from airstreams was obtained with high removal efficiency and a negligible pressure drop of the bed by using a biofilter packed with a mixture of compost–scoria–sugarcane bagasse [349].

8. Conclusions

Aldehydes are highly reactive chemical substances widely used in academia and industry and are highly present in our environment; they are largely found in cosmetics and pharmaceuticals and are widely used in plastic production, (bio)fuels, and perfumery applications. Exposure to aldehydes may occur in outdoor and indoor environments, including the workplace, and can also occur in foods and non-alcoholic beverages. Some aldehydes derive from natural sources, whereas others are synthetic. Generally, they are introduced into PCPs due to their very good scent. Over the years, extensive research has revealed the relationship between reactive aldehyde sources and the high risk of reactive aldehyde exposure, resulting in negative consequences for health. Indeed, for many of them, potential or certain toxicity has been demonstrated, which can also lead to carcinogenic effects. BMCA, for instance, has generally been withdrawn from the market in several countries. It is therefore necessary to understand whether it is better to use scented products of this type or encourage the use of less-scented products, such as perfumes of natural and non-synthetic origin, obtained from plants or with genetic and/or metabolic engineering and sustainable methods, to replace synthetically derived aldehydes. Overall, this review aims to summarize the most representative scientific observations and propose critical food for thought about the extensive use of aldehydes and their impact on the environment and, consequently, on human health.

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