MJoSHT
Malaysian Journal of Science, Health & Technology
[mjosht.usim.edu.my]

Article

Synthesis, Characterization, and Perfumery Application of Acetal Derivatives of 2-Methyl-3-(4-R-Phenyl) Propanal: A Short Review

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Article Info
Article history:
Received:23 August 2022
Accepted:30 March 2023
Published:6 April 2023

Academic Editor:
Shahrina Ismail

Malaysian Journal of Science, Health & Technology

MJoSHT2023, Volume 9, Issue No. 1
eISSN: 2601-0003

https://doi.org/10.33102/mjosht.v9i1.321

***Abstract*— Perfumes and fragrances are seen as an essential part of life in many countries, and many men and women use perfumes regularly. Originally, the perfume ingredients were derived from natural sources such as essential oils. However, these natural ingredients encountered challenges, such as poor crop quality, a limited supply of supplies, or difficulties using plant or animal extracts. Hence, with the development of synthetic organic chemistry in the 19th century, many ingredients were produced synthetically, resulting from the creativity of laboratory chemists, and used in today's perfumes. Acetal is one of the synthetic aromatic chemicals used as ingredients in perfume nowadays. This paper review focuses on synthesis and characterization techniques for analyzing acetal derivatives of 2-methyl-3- (4-R-phenyl)propanal and their perfumery application, such as odor characteristics.**

***Keywords*—** acetal derivatives, acetalization, synthesis, characterization, perfume ingredients.

I. INTRODUCTION

Many countries see perfumes and fragrances as essential to life, and many men and women use perfumes regularly. Perfumes and fragrances synthesize science and art, in which chemists become creative, and molecules create memories. Fragrances are one-of-a-kind. They are created with thought, passion, and innovation. They provide enjoyment to billions of individuals worldwide who use and appreciate perfumes daily, from fresh-smelling shampoo to freshly laundered apparel. An odor is generated by one or more volatilized chemical compounds, typically present in low concentrations, and may be detected by people and animals by their fragrance. Odors have an important function in human behavior. While a nice aroma might be comforting or make one feel better, unpleasant odors can negatively impact our mood and cause worry and pain. The significance of odors in human behavior has been extensively documented [1]. According to an insightful review, inhaling certain odorants can modify many physiological processes [2].

Perfume is a liquid mixture of fragrant essential oils or aroma compounds, fixatives, and solvents that give a pleasant odor to the human body, animals, food, items, and living environments [3]. Originally, the perfume ingredients were derived from natural sources from plant or animal products. However, these natural ingredients depend on problems like poor crop quality, lack of supplies, or difficulties using plant or animal extracts. Besides, natural sources are also typically not very stable and decompose with light, humidity, or warmth [4]. As a result, with the advent of synthetic organic chemistry in the 19th century, numerous chemicals were manufactured synthetically due to laboratory scientists' inventiveness and employment.

Carbonyl moiety is one of chemical synthesis's most prevalent and widely used functional groups. Acetal is commonly utilized in multistep chemical synthesis to shield carbonyl compounds from basic and nucleophilic reagents due to their general stability to various reagents and ease of removal. [5]. Furthermore, they have found use in everyday life as fragrances or pro-fragrances. Acetal, which is one of the synthetic aromatic chemicals, is widely used in synthetic perfumes. An acetal with two alkoxy groups, -OR attached to the same carbon, is formed when aldehyde or ketone is treated with an excess of alcohol in the presence of an acid catalyst. The mechanism includes acid-catalyzed hemiacetal synthesis, followed by acid-catalyzed water removal and adding a second alcohol group [5].

Despite recent improvements in the knowledge of the olfaction process in humans, making perfume remains mostly empirical, relying on the perfumers' expertise and know-how. Over the last several years, odor perception has been explored, such as predicting odor strength and character or discovering novel materials utilizing computer aroma design with quantitative structure-activity relationships [6]. The features of perfumes are investigated for as many structurally related compounds as possible to apply the acquired procedures to synthesize a diverse range of scents [7]. The odors of odorant compounds with the same functional group appear identical. This is because similar substances or mixtures of compounds can interact with receptors to produce similar sensory impressions in the brain's sensory centers, resulting in odor similarity [8]. However, small structural changes, on the other hand, can escalate an odor by many orders of magnitude after a sensory experience [8]. Therefore, many researchers have investigated the relationship between a compound's molecular structure and its odor [1], [6], [9]. For example, 4,4-dimethyl-2-octeno-lactone, 8-methyl-2-noneno-lactone, and 5,6,6-trimethyl-2-hepteno-lactone have the same parent group, lactone, but completely distinct scents. The first compound has a minty aroma, the second has a buttery aroma, and the third has a terpene-like and camphorous aroma [9]. This shows that even a small change in a molecule's structure or functional group can dramatically alter its odor characteristics.

Continuing prior studies of the acetal and structure-scent relationship, a review has been conducted on synthesis and characterization techniques for analyzing acetal derivatives of 2-methyl-3-(4-R-phenyl) propanal and their perfumery application.

II. NATURE OF PERFUME: NATURAL VERSUS SYNTHETIC

Perfumes are categorized as natural or synthetic based on their origin. The term perfume may be described as a preparation that produces a pleasant odor and is generally a liquid based on natural or synthetic chemicals [1]. The perfumes consist of a combination of aromatic and essential oils. They are generally composed of natural aromatic oils until the 19th century, but now most perfumes are synthetic and can produce many fragrances. When the perfume ingredients are of natural origins, such as from animals or plants, it is referred to as an extract or essential oil. On the other hand, concentrated is a more generic phrase. All these terms refer to the concentrated liquid that contains the volatile fragrance.

A. Natural Perfumes

Originally, perfume ingredients were produced naturally from plant or animal products. Plants are based on ingredients obtained from their different parts. Flowers such as roses and jasmine; leaves like lavender; fruits, seeds like anise, roots (ginger), and barks; and some woods like pines still offer enormous quantities of aromas for the perfume sector. These substances based on plants are obtained by several physical methods, including hydro distillation, solvent and Soxhlet extraction, enfleurage, maceration, and expression [10]. For animals, some of their secretions contain odorous chemicals that boost perfume propagation and characteristics or can operate as a fixative, reducing the evaporation rate of the most volatile perfume ingredients. Examples include ambergris, castor, civet, and musk [10]. Alcohol maceration extracts natural compounds from animal products [10]. However, these natural ingredients depend on problems like poor crop quality, lack of supplies, or difficulties using plants or animals.

B. Synthetic Perfumes

Due to some problems natural ingredients face, such as high cost and lack of supplies, modern perfumes use synthetic ingredients as synthetic organic chemistry grew in the 19th century. Synthetic perfumes combine fragrance molecules created in a laboratory to create an odor comparable to a natural smell or to find something new and unique. These synthetic chemicals arose because of the great demand for fragrances in the twentieth century, which increased their cost while decreasing the availability of some of them for ethical or safety concerns. Synthetically, volatile compounds with slightly changed structures with more desired characteristics, such as better stability, are developed [4]. Moreover, the most significant thing is the cost efficiency of perfume ingredient production. Therefore, synthetically produced acetals are commonly used in today's perfume. In addition to new scent notes, synthetic changes in the chemical structures of natural substances can provide more stable scent components or chemicals without health issues [4].

For example, in previous research by Shahzadi et al. [11], the acetal compound seems stable to be used as a fragrance instead of a natural aldehyde. On the other hand, citral, an aldehyde extracted from lemongrass, is a perfume with a strong lemon scent added to the essential oils of natural lemon. However, it is volatile to air, sunrays, and alkalis, barely maintaining its scent. Citral dimethyl acetal and citral diethyl acetal have been utilized to fix this problem, but such chemicals have no lemon scent. Instead, it produces a neroli-like citrus-green aroma, thus having no lemon-like citral aroma [11]. This explains that acetal, as a synthetic structure, can form a new odor note in addition to more stable aromas. In another research by Sekerova et al. [12], 5-methyl-5-propyl-2-(1- methylbutyl)-1,3-dioxane is also one of the examples of acetal as a synthetic structure that is used as a perfume ingredient. The fragrance properties of this compound were described as tulip flower, a note of privet bloom, a deep green, and an oily texture [12].

III. ACETAL AND KETAL AND THEIR DERIVATIVES

A. Acetal, Ketal, and The Derivatives

An acetal (Fig. 1) or a ketal (Fig. 2) with two alkoxy groups, -OR linked to the same carbon, occurs in the presence of an acid catalyst when aldehyde or ketone is treated with an excess of alcohols [5]. The acetal and ketal are functional groups with a general formula of $R_2C(OR')_2$. For acetal, from the general formula, the R can be any alkyl group or hydrogen (H), while the R' group must be an alkyl group and not hydrogen. However, it differs for ketal, where both R groups must be alkyl rather than H. The term acetal is used specifically to identify structures associated with aldehyde, while the term ketal describes structures associated with ketone.

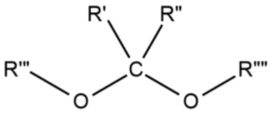


Fig. 1: Structure of acetal

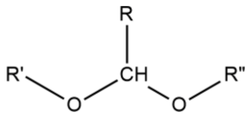


Fig. 2: Structure of ketal

The organic process involving acetal or ketal formation is called acetalization. Typically, acetalization is an acid-catalyzed reaction between alcohols and carbonyl compounds, either aldehyde or ketone [12]. The process begins with synthesizing acid-catalyzed hemiacetal and acid-catalyzed water, then adding the second group of alcohols. Industrial processes are usually catalyzed by strong acids such as *p*-toluenesulfonic acid, sulfuric acid, phosphoric acid, hydrochloric acid, and resin exchange [12]. In addition, a wide range of homogeneous and heterogeneous catalysts can be utilized for acetalization catalytic, including Lewis and Bronsted acids such as heteropoly acids, zeolites, metal oxides, ionic liquids, and modified activated carbons [12]. Moreover, acetals can be used as protecting groups of carbonyl functional groups. Due to the stability of acetals in most conditions that do not involve acid, they can protect aldehydes and ketones from undesirable reactions in basic solutions. [5]. When no longer needed, the acetal group can then be removed by acidic hydrolysis. On the other hand, acetals may also be employed in many syntheses, be helpful intermediates, or be used in diverse products, such as perfumes, cosmetics, food and drink additives, drugs, detergents, and lacquers [12]. The fragrance of acetals generated from aliphatic aldehydes is weaker when characterized by resource aldehydes. Furthermore, aliphatic acetals are utilized in perfumes rather than aldehydes due to their stability against oxidation [12].

Cyclic acetals with a varying number of atoms can be created depending on the structure of the substrate structures. By reacting to polyol with suitable aldehydes or ketones, cyclic acetals (Fig. 3) or cyclic ketals (Fig. 4) are formed [13]. For example, glycerol reacts with ketones forming 5 atoms in the cycle, known as 1,3-dioxolanes while glycerol reacts with aldehydes forming 6 atoms in the cycle, known as 1,3-dioxanes. The literature contains a wide range of cyclically scented acetals [12]. Due to their stability and safety, cyclic acetals were classed as stable and potentially applicable in the perfume industry.

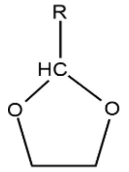


Fig. 3: Cyclic of acetal

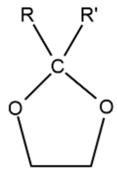
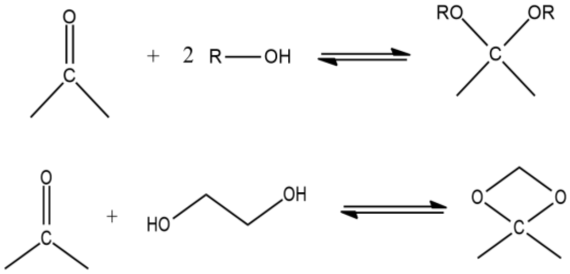


Fig. 4: Cyclic of ketal

The reaction of monohydric alcohols such as methanol and ethanol with aldehyde or ketone will form an aliphatic acetal or ketal, while the reaction of diols such as ethylene glycol with aldehyde or ketone will form a cyclic acetal or ketal. Scheme 1 presents the chemical reaction of synthesizing ketal and cyclic ketal.



Scheme 1: Chemical reaction on synthesizing ketal and cyclic ketal

The required acetal or ketal derivatives can be designed by the substituents in the reaction with aldehyde or ketone. In addition, the characteristics of aroma, vapor pressure, flavor, and solubility can be modified using different carbonyl compound conversion methods.

In previous research, citral acetal, known as citral propylene glycol acetal (Fig. 5), has been synthesized from citral extracted from lemon grass and alcohol [11]. Citral acetals are significant intermediates for flavor production and their usage in fragrances and cosmetics.

Besides, in another research by Kumar et al. [14], a fuel additive, 5-hydroxymethyl furfural acetal (Fig. 6), was synthesized from 5-hydroxymethyl furfural (5-HMF) and 1,3-propanediol using a synthesis laboratory. The 5-HMF acetalization will be particularly valuable for developing a green process path to turn waste biomass and using platform molecules obtained into potentially usable acetal products [14].

The other derivative of acetal is para-methane-3,8-diol citronellal acetal (Fig. 7), which was synthesized from citronellal and para-methane-3,8-diol (PMD) extracted from the tree, Eucalyptus citriodora [15]. This acetal can be used as a bio-plasticizer for cosmetic purposes. Eucalyptus oil, with beneficial properties such as antimicrobial, antifungal, anti-inflammatory, antiseptic, and bactericidal properties, contains two interesting compounds: PMD and citronellal [15]. Both compounds in Eucalyptus oil naturally synthesize PMD-citronellal acetal.

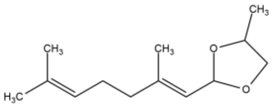


Fig 5: Citral propylene glycol acetal

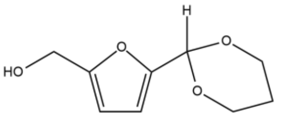


Fig. 6: 5-hydroxymethyl furfural acetal

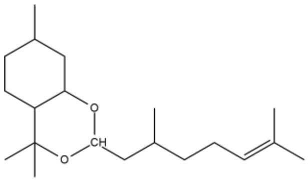


Fig. 7: *para*-methane-3,8-diol citronellal acetal

B. *Mechanism of Formation of Acetal*

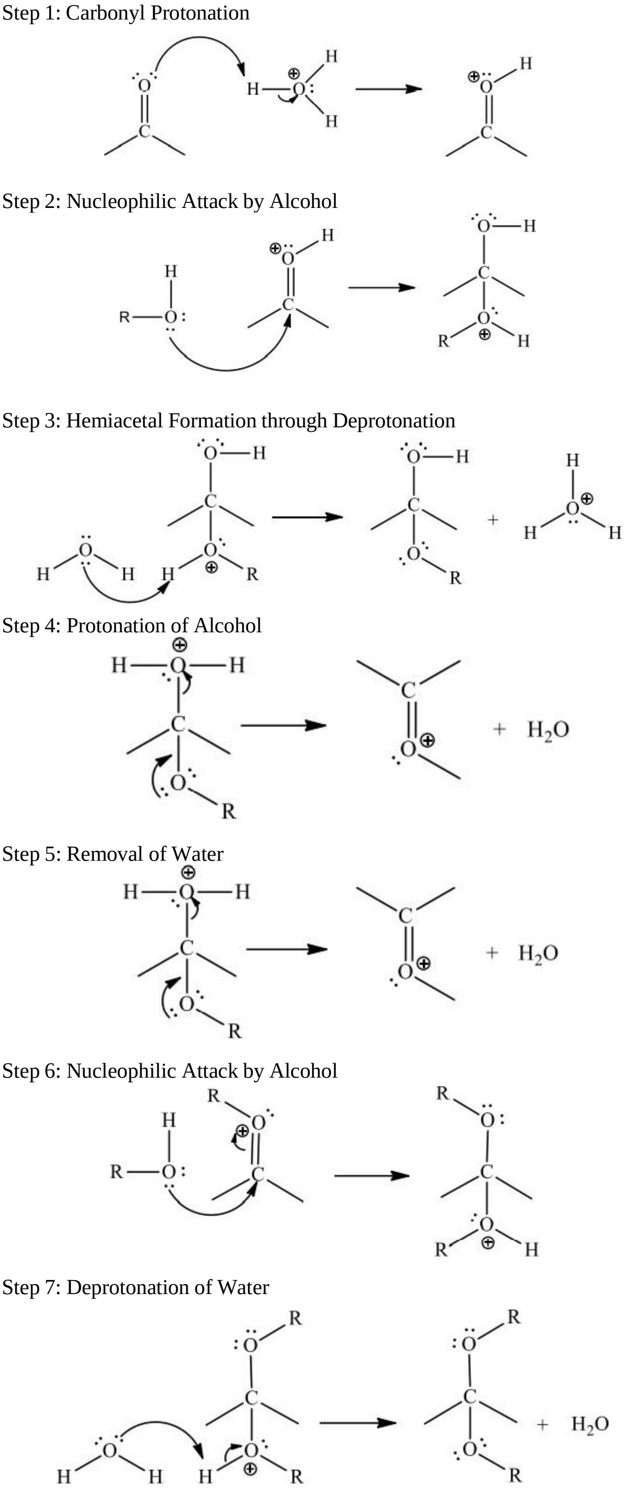
Acetal formation is a reversible process that occurs in a two-step mechanism. The hemiacetal formation is the first step, followed by removing water molecules as the second step. Scheme 2 provides the general mechanism without any conditions for the reaction. There are seven steps of the general mechanism for hemiacetal and acetal formation [5].

C. *Synthesis of Acetal Derivatives*

Acetals can be utilized as key components in new synthetic applications. For example, acetals are utilized as flavor and aroma enhancers in cosmetics and food, anti-freezing additives in biodiesel fuels, and chemically manufactured uses [16]. Due to their versatility, acetals have been synthesized using several methods. The most common method employs strong minerals, transition metal Lewis, or organic acids.

However, using a stoichiometric quantity of acids or metals raises major environmental problems, breaking green chemistry standards [16]. Hence, alternative procedures for the acetalization of organic molecules have been designed to overcome this issue. Acetals can be synthesized from carbonyl compounds under basic or non-acidic conditions using iodine [17], trialkyl orthoformates, or halohydrins. In previous research by Vyglazov et al. [7], they synthesized the aldehydes and alcohols produced acetal derivatives using a method where the catalyst used is a fibrous sulfonic cation exchanger (FIBAN K-1).

Besides, a technique for synthesizing acetals based on photochemistry principles was recently developed [16]. In connection with that, a new photo-organocatalytic synthesis of acetals from aldehydes has been described as green, mild condition, and fast. This method utilized photo-organocatalyst and household lamp as irradiation source since it is inexpensive and commercially available. Based on research by Nikitas et al. [16], the product produced from this method has a high percentage yield, and the reaction time is very short. This is due to the formation of the EDA complex upon adding the aldehyde to the photo-organocatalyst. After irradiation activates the aldehyde via energy transfer, like how a Lewis acid activates the aldehyde, lowering the LUMO of the aldehyde and making it more vulnerable to the upcoming nucleophilic attack of alcohol can result in the corresponding acetal.


Step 1: Carbonyl Protonation

Step 2: Nucleophilic Attack by Alcohol

Step 3: Hemiacetal Formation through Deprotonation

Step 4: Protonation of Alcohol

Step 5: Removal of Water

Step 6: Nucleophilic Attack by Alcohol

Step 7: Deprotonation of Water

Scheme 2: Mechanism of hemiacetal and acetal formation [5].

The catalyst then reverts to its ground state after reacting with molecular oxygen, while the radical oxygen species created enhance radical propagation and product synthesis. The pure product then may be acquired through solvent evaporation or distillation using Dean stark apparatus.

D. The Use of Catalyst during Synthesis

Typically, acetalization is an acid-catalyzed reaction between alcohols and carbonyl compounds, either aldehyde or ketone [12]. The process comprises the formation of acid-catalyzed hemiacetal and acid-catalyzed water, followed by adding the second group of alcohols. Industrial processes are usually catalyzed by strong acids such as *p*-toluenesulfonic acid [18], sulfuric acid, phosphoric acid, hydrochloric acid, and resin exchange [12]. For example, in previous research by Burger [15], concentrated sulfuric acid was employed as a catalyst in a reaction between citronellal and *para*- methane-3,8-diol to produce *para*-methane-3,8-diol citronellal acetal. The product produced has a 74% percent yield. In another research, Shahzadi and his co-researchers [11] utilized *p*-toluenesulfonic acid as a catalyst to synthesize citral and propylene glycol forming citral propylene glycol acetal. However, common acid catalysts such as hydrochloric acid, sulfuric acid, *p*-toluenesulfonic acid, and trifluoroacetic acid are corrosive when employed to produce ketals or acetals by reacting aldehydes or ketones with alcohols [19].

A wide range of homogeneous and heterogeneous catalysts can be utilized for acetalization catalytic, including Lewis and Brønsted acids such as heteropoly acids, zeolites, metal oxides, ionic liquids, and modified activated carbons [12]. Research by Kumar and his co-researchers [14] applied Brønsted acidic IL ([IL-SO_3H] [CF_3SO_3]) catalyst in their synthesis to form 5-hydroxymethyl furfural acetal (5-HMF acetal) from 5-hydroxymethyl furfural (5-HMF) and 1,3- propanediol. From this synthesis, at 313.15 K and 150 min of reaction time, 99.20% of 5-HMF conversion and 87.50% of 5-HMF-cyclic acetal selectivity were achieved. Besides, pyridinium salt derivatives [20], dialkyltriazolium salts [21], and imidazolium salts [22] are aprotic salts that can act as Brønsted acids in chemo selectively acetalization. Ammonium salts are utilized as heterogeneous catalyst for the acetalization of aldehydes, according to research by Azzena and co-researchers [23], because it is ecologically safe, inexpensive, widely accessible, and mild heterogeneous acidic catalysts.

For the photo-organocatalytic synthesis of acetals, photocatalysts are utilized as catalysts to synthesize the acetal derivatives. Aromatic ketones, in general, are major participants in this form of catalysis, as evidenced by various examples in the literature [24]. Among the aromatic ketones, thioxanthone (TX) appears to have a distinctive function in photochemistry. When compared to other aromatic ketones, TX has a high triplet energy and a relatively long triplet lifespan, and it has the potential to participate well in merger processes with metal complexes [24]. Moreover, it is used as a mediator, particularly in polymerization processes and organic conversions. Based on previous research by Nikitas [16], several photo-organocatalysts were evaluated, with thioxanthone providing the best yield of over 95%. Since photo-organocatalytic synthesis will be applied in this reaction, thioxanthone is a better catalyst to be employed. Table I lists the catalysts that have been used for acetalization.

TABLE I. CATALYSTS FOR ACETALIZATION

Catalysts	**References**
p-toluenesulfonic	[11], [18]
Sulfuric acid	[12], [15]
Phosphoric acid	[12]
Hydrochloric acid	
Resin exchange	
Heteropoly acids	
Zeolites	
Metal oxides	
([IL-SO_3H] [CF_3SO_3])	[14]
Pyridinium salt derivatives	[20]
Dialkyltriazolium salts	[21]
Imidazolium salts	[22]
Ammonium salts	[23]
Thioxanthone	[16], [24]

E. The Use of Solvent during Synthesis

While much effort has been devoted to searching for low-impact, heterogeneous, and recyclable catalysts to generate these reactions, significantly less work has been expended on their use in low-impact solvents. Indeed, under Dean-Stark conditions, acid-catalyzed acetalization processes are often carried out using potentially hazardous hydrocarbon solvents such as toluene or benzene. In previous research, Vyglazov and his co-researchers [7] employed benzene as a solvent in their synthesis to dissolve the carbonyl compound and alcohols to reduce the cost of the acetalization process. Nonetheless, benzene is highly volatile, and exposure occurs mostly through inhalation. Benzene seems harmful because exposure to benzene is linked with various severe and long-term detrimental health consequences, including cancer and aplastic anemia [25]. Ferreira [26] investigated iron(III) porphyrin’s catalytic activity for acetalization using carbon tetrachloride as one of the solvents, and the solvent usage indicates no product in the reaction since it is a non-polar solvent. Furthermore, carbon tetrachloride has been identified as a substance that might cause liver damage due to its hazardous metabolites [27].

Besides, Tanaka and his colleagues [28] discovered that using dichloromethane as a solvent for the regioselective ring-opening of benzylidene acetal may provide up to 83% yield. Apart from that, cyclohexane is a very effective and efficient solvent. The use of solvents in both processes of carbonyl compound protection as 1,3-dioxalanes and carbonyl compound protection as dialkyl acetals using indium(III) chloride as a catalyst in both reactions may generate more than 80% of the percentage yield [29]. In addition, it may produce an azeotropic combination of cyclohexane and water, and according to Le Chatelier’s Principle, it will favor the product [30] if the substituent ratio is greater than the starting material. However, acetalization does not occur at a 1:1 ratio between 2-methylpentanal and 2-methyl-2-propyl- 1,3-propanediol utilizing cyclohexane, hexane, heptane, and 1,4-dioxane as solvents. Due to low dielectric constant values in the solvents and 2-methyl-2-propyl-1,3-propanediol, their solubility was poor [12].

To develop reaction methods that involve ecologically friendly solvents, according to research by Azzena and co-workers [24], cyclopentyl methyl ether (CPME) [31] and 2-methyltetrahydrofuran (2-MeTHF) [32] were used to study the acetalization of aldehydes and ketones in widely known low impact ethereal solvents that form positive azeotropes with H_2O. Both CPME and 2-MeTHF show the ratio of solvent: H_2O are 83.7:16.3 and 89.4:10.6, respectively. Both CPME and 2-MeTHF have relatively high acid and base stability, as well as low toxicity [33], [34], relatively high boiling points, a narrow explosion range, hydrophobicity, easy drying, and recovery, and seem to be versatile green alternatives to ethereal solvents like tetrahydrofuran, diethyl ether, or tert-butyl methyl ether [23]. Furthermore, CPME is created by a 100 percent atom economical process [35], while 2-MeTHF is derived from renewable resources [36]. Table II presents the red solvents and their alternative and green solvents for acetalization synthesis.

TABLE II. SOLVENTS FOR ACETALIZATION

Solvents		**References**
Types of Solvents	**Solvents Name**	
Red Solvents	Benzene	[7]
	Carbon tetrachloride	[26], [27]
	Tetrahydrofuran	[23]
	Diethyl ether	
Alternativ eSolvents	Dichloromethane	[28]
	Cyclohexane	[29]
Green Solvents	Cyclopentyl methyl ether (CPME)	[31], [35]
	2-methyltetrahydrofuran (2-MeTHF)	[32], [36]

IV. CHARACTERIZATION

A. *Fourier Transform Infra-Red (FTIR) Spectroscopy*

Fourier Transform Infrared (FTIR) Spectroscopy is an essential analytical method for analyzing diverse substrates. FTIR is a technique that obtains solid, liquid, and gas infrared absorption, emission, and photoconductivity spectrum [37]. It is used to detect different functional groups in organic compounds. The infrared spectra of acetals and ketals are observed in the 3000 and 1400 cm^{-1} regions [38]. On the other hand, the FTIR spectra exhibit a characteristic acetal pattern consisting of five bands in the range 1185-1030 cm^{-1} [7]. In previous research by Shahzadi et al. [11], citral ethylene glycol acetal exhibits several functional groups in the FTIR spectrum, such as C-O, C=C, and C-H groups. The peak of the C=C group is shown at 1665 $cm^{-1,}$ while the C-O group’s peak appeared at 1220-1100 cm^{-1}. On the other hand, the peaks of C-H stretching were recorded at 3649 cm^{-1}, 2924 cm^{-1}, 2867 $cm^{-1,}$ and 1460 cm^{-1}. Table III presents the IR frequency range and band assignment of acetal derivatives.

B. *Nuclear Magnetic Resonance (1H NMR) Spectroscopy*

Nuclear Magnetic Resonance (NMR) is a physical system that absorbs and remits magnetic radiation in the magnetic field [37]. It is a method for spectroscopic observation of local magnetic fields surrounding nuclear nuclei. In previous research by Vyglazov et al. [7], a characteristic doublet at 4.3-4.8 ppm corresponds to the $HC(OR)_2$ in the ^1H NMR spectra. In another research by Pawar et al. [39], the acetalization of glycerol with benzaldehyde produced 1,3-dioxolane. The proton shifts of this compound are shifted at 5.77 and 5.90 ppm in ^1H NMR spectra. The range of ^1H NMR chemical shift of the acetal derivatives compounds is shown in Table IV.

C. *CHNS Elemental Analysis*

Elemental analysis is a technique that analyses a sample of certain materials such as soil, waste or drinking water, body fluids, minerals, and chemical compounds for their elemental and occasionally isotopic composition. Elemental analysis is necessary to confirm 95% sample purity and isomeric purity. This information is useful for determining the structure of an unknown chemical and the synthesized compound’s structure and pureness. In the CHNS analyzer, the organic component is oxidatively decomposed and then reduced with the production of final products by nitrogen and sulfur oxide: carbon dioxide, water, elemental nitrogen, and sulfur dioxide [40]. Table V shows each acetal derivatives compound’s carbon and hydrogen elements percentage.

TABLE III. IR FREQUENCY RANGE AND BAND ASSIGNMENT OF ACETAL DERIVATIVES

Compounds	**Band Assignment (cm^{-1})**			**References**
	v (C-O)	**v (C=C benzene)**	**v (C-O methoxy)**	
2-methyl-3-(4-methylphenyl)propanal dimethylacetal	1150–1050	1490-1420	2820-2810	[7], [11]
2-methyl-3-(4- isopropylphenyl)propanal dimethylacetal	1150–1050	1480-1430	2820-2810	
2-methyl-3-(4-tert- butylphenyl)propanal dimethylacetal	1150–1050	1500-1430	2820-2810	
2-methyl-3-(4- methylphenyl)propanal ethylene acetal	1140–1070	1490-1420	-	
2-methyl-3-(4- isopropylphenyl)propanal ethylene acetal	1140–1070	1480-1430	-	
2-methyl-3-(4-tert-butylphenyl)propanal ethyleneacetal	1140–1070	1500-1430	-	

TABLE IV. RANGE OF ^{1}H NMR CHEMICAL SHIFT OF THE ACETAL DERIVATIVES

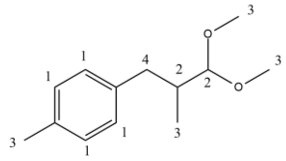
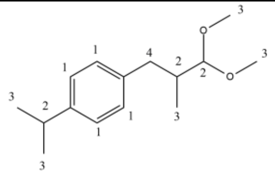
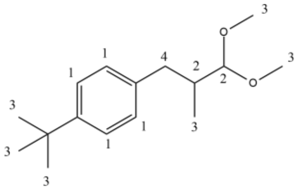
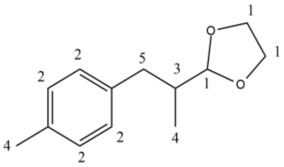
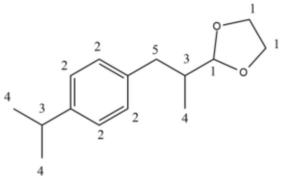
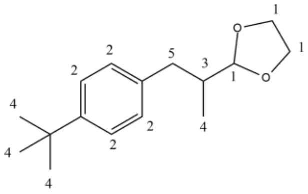
Compounds	**Assignment**	**^{1}H NMR Chemical Shift Range, δ (ppm)**	**References**
 2-methyl-3-(4-methylphenyl)propanal dimethyl acetal	δ_{H1} (Benzene)	6.98-7.18	[7], [40]
	δ_{H2} (Methine)	2.69-4.18	
	δ_{H3} (Methyl)	0.96-3.50	
	δ_{H4} (Methylene)	2.38-2.63	
 2-methyl-3-(4-isopropylphenyl)propanal dimethyl acetal	δ_{H1} (Benzene)	7.02-7.25	
	δ_{H2} (Methine)	2.69-4.18	
	δ_{H3} (Methyl)	0.96-3.50	
	δ_{H4} (Methylene)	2.38-2.63	
 2-methyl-3-(4-tert-butylphenyl)propanal dimethyl acetal	δ_{H1} (Benzene)	7.02-7.41	
	δ_{H2} (Methine)	2.69-4.18	
	δ_{H3} (Methyl)	0.96-3.50	
	δ_{H4} (Methylene)	2.38-2.63	
	δ_{H1} (1,3-dioxolane)	3.95-4.88	
 2-methyl-3-(4-methylphenyl)propanal ethylene acetal	δ_{H2} (Benzene)	6.98-7.18	
	δ_{H3} (Methine)	2.65-2.71	
	δ_{H4} (Methyl)	0.96-2.34	
	δ_{H5} (Methylene)	2.38-2.63	
 2-methyl-3-(4-isopropylphenyl)propanal ethylene acetal	δ_{H1} (1,3-dioxolane)	3.95-4.88	
	δ_{H2} (Benzene)	7.02-7.25	
	δ_{H3} (Methine)	2.69-2.87	
	δ_{H4} (Methyl)	0.96-1.20	
	δ_{H5} (Methylene)	2.38-2.63	
 2-methyl-3-(4-tert-butylphenyl)propanal ethylene acetal	δ_{H1} (1,3-dioxolane)	3.95-4.88	
	δ_{H2} (Benzene)	7.02-7.41	
	δ_{H3} (Methine)	2.65-2.71	
	δ_{H4} (Methyl)	0.96-1.35	
	δ_{H5} (Methylene)	2.38-2.63	

TABLE V. PERCENTAGE OF CARBON AND HYDROGEN ELEMENTS IN EACH ACETAL DERIVATIVES COMPOUNDS

Compounds	**Chemical Formula**	**Element Composition (%)**		**References**
		C	**H**	
2-methyl-3-(4-methylphenyl)propanal dimethyl acetal	$C_{13}H_{20}O_2$	74.53 (74.96)	9.17 (9.68)	[7]
2-methyl-3-(4-isopropylphenyl)propanal dimethyl acetal	$C_{15}H_{24}O_2$	76.04 (76.23)	10.08 (10.24)	
2-methyl-3-(4-tert-butylphenyl)propanal dimethyl acetal	$C_{16}H_{26}O_2$	76.43 (76.75)	10.16 (10.47)	
2-methyl-3-(4-methylphenyl)propanal ethylene acetal	$C_{13}H_{18}O_2$	75.46 (75.96)	8.37 (8.80)	
2-methyl-3-(4-isopropylphenyl)propanal ethylene acetal	$C_{15}H_{22}O_2$	76.67 (76.88)	9.22 (9.46)	
2-methyl-3-(4-tert-butylphenyl)propanal ethylene acetal	$C_{16}H_{24}O_2$	77.11 (77.38)	9.57 (9.74)	

V. PERFUMERY APPLICATION

A. *Odor Characteristics*

Perfumes and essential oils can be categorized according to their fragrances. As a result, many notes such as floral, citrus, fruity, green, woody, oriental, spice, animal, and leather can be discovered [1]. In addition, over the last several years, odor perception has been explored, such as in predicting odor strength and character or in discovering novel materials utilizing computer aroma design with quantitative structure-activity relationships [6]. The link between a chemical compound's molecular structure and its odor quality or strength is particularly interesting. The biggest issue when using structural activity is a lack of understanding of the olfactory process and the imprecision of odor measurement related to odor description and intensity [41]. The first issue is connected to the odorant's molecular recognition by the G-proteins. Two molecular characteristics have been considered significant: the molecule shape and the form and arrangement of its functional groups. The second issue is that it relies on human perception, which may be very subjective.

On the one hand, odor perception is the outcome of physiological interactions that rely on an impression or connection from the person's prior experience. On the other hand, people's ability to recognize diverse odor descriptors is restricted due to insufficient expertise or vocabulary to explain the odor detected [41]. In this regard, fragrance specialist Michael Edwards created his fragrance categorization method in 1983, considering the odor that a fragrance offered, which is still used as a reference today [1]. The fragrance wheel is a classification chart designed to make fragrance categorization and naming methods easier to understand. As a reference vocabulary, several standard odor descriptors list accessible [42]. For example, an odor wheel (Fig. 8) represents eight recognized odor descriptor categories: Vegetable, Fruity, Floral, Medicinal, Chemical, Fishy,Offensive, and Earthy.

Odor measuring has been the topic of much research in the flavor and fragrance industries for many years. However, choosing a suitable measuring approach to characterize odor performance is still difficult, which is a significant success factor in addition to excessive features. For many years, physicochemical parameters have been used to generate guidelines for improving perfume performance. However, headspace measurements coupled with olfactometry data remain among the most powerful method to extract additional information by connecting detected signals acquired from a device with the sensory perception of a human nose [43]. Machine olfaction has been a relatively new technology in the works for years. The electronic nose with an array of gas sensors, which can perceive odorous molecules and odorless chemicals, is an essential application form of machine olfaction. In addition, electronic noise has been used in scientific and commercial applications such as environmental monitoring, food processing inspection, and perfumery application due to its quick reaction, portability, and ease of use [44].

B. *Aroma/odor-structure relationship*

The molecule's chain length and functional group are important elements in odor characteristics. Previous research by Buchbauer [45] has studied the structure-odor relationship on sandalwood odor compounds. A unique issue of these investigations is that even minor structural changes to a sandalwood odor molecule result in the entire loss of scent, even though numerous substances with completely different chemical structures possess sandalwood fragrance. The functional group, a methyl group nearby, and sections of the bulky aliphatic residue represent the osmophoric sites [45]. The fragrance is caused by steric and electrostatic characteristics, as evidenced by changes to the parent chemical. Furthermore, the olfactory impressions of optical isomers differ greatly. For example, the aroma of α, β- unsaturated aldehyde may be described as pleasant cistus and e-iris-root-like with an animal fatty tonality, while the odor of its saturated aldehyde can be described as green and woody [45].

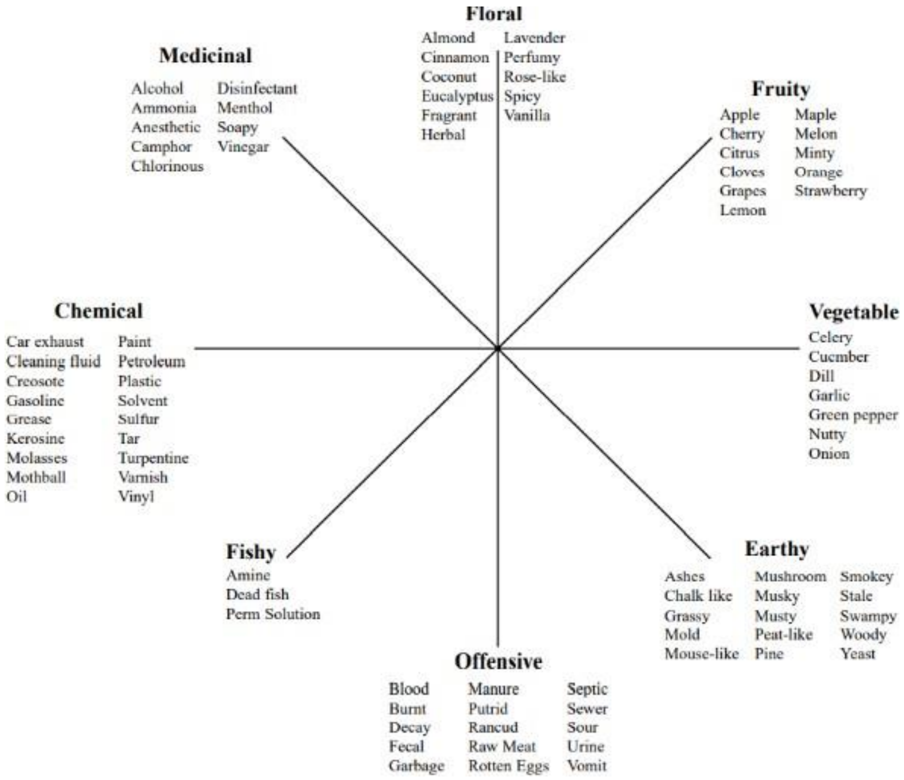


Fig. 8. Odor Descriptor Wheel [43].

TABLE VI. THE FRAGRANCE OF ACETAL DERIVATIVES OF 2-METHYL-3-(4-R-PHENYL) PROPANAL

Compounds	Odor Characteristics
2-methyl-3-(4-methylphenyl)propanal dimethylacetal	Green, flowery, with a bittery tint
2-methyl-3-(4-isopropylphenyl)propanal dimethylacetal	Green, of cyclamen, with a bitter grassynote
2-methyl-3-(4-tert-butylphenyl)propanal dimethylacetal	Strong, flowery, with a cold note of cyclamen and lily of the valley, lightozone
2-methyl-3-(4-methylphenyl)propanal ethyleneacetal	Flower-grassy with a tint of parsley,celery, and anise
2-methyl-3-(4-isopropylphenyl)propanal ethyleneacetal	Flowery, of cyclamen, with a fresh watermelon note
2-methyl-3-(4-tert-butylphenyl)propanal ethyleneacetal	Flowery, of cyclamen, with a sweet anisenote

According to another study by Lubes [41], changing the functional group affects the odor threshold of molecules with identical structures. The odor of aliphatic or aromatic alcohol can be changed or even eliminated by shifting the position or withdrawing the hydroxyl group, as in terpenes and terpenoids [46]. For example, limonene has a citrus, orange-like odor, while carveol, its oxidized form, has a more minty aroma [47]. Table VI presents the scents of acetal derivatives of 2-methyl-3-(4-R-phenyl) propanal as described in research by Vyglazov [7] related to the structure-scent relationship in the series of acetals.

VI. CONCLUSION

A basic, economical, green, and effective photo-organocatalytic technique was established to boost aldehydes to interact with alcohols to produce acetals. This method, which avoids the use of transition metal-complexes and stoichiometric acids, depends on a small organic molecule and inexpensive household lamps to activate aldehydes via EDA-complexes, which are quick to react with alcohols to produce acetals in high yields and then may be isolated via solvent evaporation or distillation.

The acetalization of aldehydes and alcohols may be undergoing in green ethereal solvents, perhaps CPME and 2- MeTHF, in the presence of an inexpensive household lamp as an irradiation source and thioxanthone as photocatalysis. It has high triplet energy and a reasonably long triplet lifetime compared to other aromatic ketones. CPME and 2-MeTHF effectively enhanced the acetalization of various aldehydes and ketones with diols.

For the fragrance of the acetal derivatives of 2-methyl-3-(4-R-phenyl) propanal, it can be concluded that the fragrance of the acetals with similar monohydric alcohols changes gradually depending on the phenyl ring substituent. At the same time, the aroma changes more intensely as the diol series continues.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

ACKNOWLEDGEMENT

The authors would like to thank the Faculty of Science and Technology, Universiti Sains Islam Malaysia, for all the support to complete this review.

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