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SELECTIVE AND EFFICIENT OXIDATION OF UNSATURATED ALCOHOLS AS CONSTITUENTS IN ESSENTIAL OILS

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ABSTRACT

Essential oil unsaturated alcohols have been oxidized efficiently into the corresponding unsaturated aldehydes by potassium permanganate supported copper(II) sulfate pentahydrate. Unsaturated aldehydes such as geranial and cinnamaldehyde being valuable components in food, cosmetic, perfumery and pharmaceutical chemistry, have been obtained in good yields (> 60%) under two activation methods: microwave irradiation and conventional heating.

Keywords: potassium permanganate, copper(II) sulfate, microwave irradiation, unsaturated alcohol.

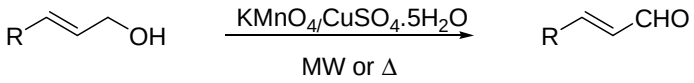
1. INTRODUCTION

The selective oxidation of alcohols into aldehydes or ketones is one of the most important transformations in organic syntheses [1], especially the oxidation of unsaturated alcohols into the corresponding unsaturated carbonyl compounds, *e.g.* the conversion of geraniol or nerol into geranial or neral, and the conversion of cinnamyl alcohol into cinnamaldehyde. These generated unsaturated aldehydes are important intermediates for the production of perfumes, fragrances and pharmaceuticals [2, 3].

Various oxidants have been proposed for the oxidation of unsaturated alcohols, for instance lead tetraacetate [4], potassium permaganate in alkaline media or supported by bentonite/$CuSO_4 \cdot 5H_2O$ in the presence of solvent [5, 6], *N*-methylmorpholine *N*-oxide catalysed by $RuCl_3$ in dimethylformamide [7], and tetrapropylammonium perruthenate (TPAP) were studied [8]. From both economics and environmental viewpoints, green oxidants have been paid attention and developed by using molecular oxygen catalyzed by sodium nitrite and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [9], or in supercritical carbon dioxide [10, 11], using hydrogen peroxide with solid catalysts and supports, [12-14] and using 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate with silica gel [15, 16].

In continuation of our works on transformation of natural compounds into valuable compounds for laboratory as well as industry, we have selected potassium permanganate absorbed on copper(II) sulfate pentahydrate, called **xPP/yCSP** (x molar amount of potassium

permanganate adsorbed on y molar amount of copper(II) sulfate pentahydrate) as oxidant for the solvent-free oxidation of natural unsaturated alcohols, typical geraniol and cinnamyl alcohol into geranial and cinnamaldehyde under conventional heating or microwave irradiation (Scheme 1). Potassium permanganate is a powerful, commercially available, in-expensive and green oxidant [17, 18], however its oxidation ability is prohibited owing to its less solubility in water and in organic solvent. In order to overcome this problem, copper(II) sulfate pentahydrate was selected to be solid support, Lewis acid and water resource. Very importantly, $KMnO_4$ absorbed on copper (II) pentahydrate is very easy to handle and safe for use, moreover removal of manganese dioxide after reaction accomplishment is carried out more easily [19].



Scheme 1. Solvent-free and selective oxidation of unsaturated alcohols into the corresponding aldehydes by potassium permanganate adsorbed on copper(II) sulfate pentahydrate.

2. MATERIALS AND METHODS

2.1. Instrumentation and chemicals

2.1.1. Instrumentation

Microwave irradiations were generated by means of a Maxidigest MX-350 microwave oven. GC/MS analyses were performed on Hewlett Packard 6890N and GC analyses were performed on Shimadzu GC-17A.

2.1.1. Chemicals

- All chemicals used were from Sigma-Aldrich.

- Typical preparation of $KMnO_4/CuSO_4 \cdot 5H_2O$: Copper(II) sulfate pentahydrate (0.12 mol, 30.0 g) was dissolved completely in de-ionized water. Then, $KMnO_4$ (0.03 mol, 4.74 g) was added, followed by a sufficient volume of de-ionized water to obtain a homogeneous solution. The solution was stirred for 10 minutes at 80^oC. Subsequently, water was removed from the solution by rotational evaporation, until the weight of the remaining solid mass was equal to the sum of the weights of the original ingredients. The obtained solid mass was ground in a mortar into a fine homogeneous powder of **PP/4CSP** [19].

2.2. Typical procedures

A test tube (h = 15.0 cm, d = 1.2 cm) containing a suitable quantity of finely ground PP/4CSP and the unsaturated alcohol (following the molar ratio as in Table 1 and 2) were placed in Maxidigest microwave oven. For each experiment, the irradiation program was applied to determine the most efficient reaction conditions, see Table 1 and 2. Subsequently, the reaction was extracted with diethyl ether (4 x 15 mL) and filtered through celite layer (2 cm). The extract was removed solvent by rotational evaporation, and then, the remaining crude product was analyzed by GC-FID and GC-MS.

The identity and purity of geranial and cinnamaldehyde reported were ensured by GC/MS and GC-FID. Because their spectroscopy data are well known, a further presentation and discussion of the spectra is not necessary.

3. RESULTS AND DISCUSSION

3.1. Oxidation of geraniol into geranial

Initially, geraniol was selected as typical unsaturated alcohol for the oxidation by potassium permanganate adsorbed on copper(II) sulfate pentahydrate under two activation methods: microwave irradiation and conventional heating. Based on the previous literature, the efficiency of copper(II) sulfate pentahydrate supported $KMnO_4$ oxidant also depends on the molar ratio between potassium permanganate and copper(II) sulfate pentahydrate [19]. Further experiments demonstrated that the molar ratio between $KMnO_4$ and $CuSO_4{\cdot}5H_2O$ in $KMnO_4/CuSO_4{\cdot}5H_2O$-promoted solvent-free oxidation of geraniol into geranial to take place most efficiently is 1:4 (Figure 1). The appropriate molar ratio of potassium permanganate and copper(II) sulfate pentahydrate chosen was found compatible with that reported in the literature on the oxidation of alcohol by PP/4CSP [19].

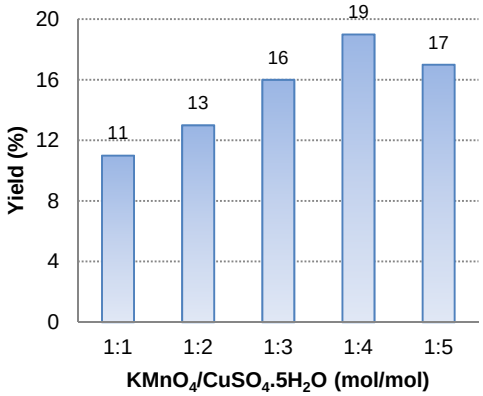
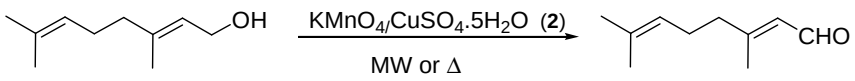


Figure 1. Influence of the molar ratio between $KMnO_4$ and $CuSO_4{\cdot}5H_2O$ in $KMnO_4/CuSO_4{\cdot}5H_2O$ on the efficiency of the oxidation of geraniol into geranial under solvent-free conditions assisted by microwave irradiation at 45 W for 10 min (geraniol: 3 mmol, $KMnO_4$: 3 mmol).

This oxidant, in the following referred to as PP/4CSP was chosen as the standard oxidant in our subsequent experiments. Initially, based on the reaction equation, the molar ratio of geraniol and PP/4CSP was selected at 3:2; however, the reaction conversion was converted incompletely. A series of experiments on the molar ratio between geraniol and PP/4CSP were performed by varying the molar ratios sequentially at 45 W for 10 minutes under microwave irradiation (Entry 1-6, Table 1). The results displayed that using an appropriate amount of PP/4CSP increased the reaction conversion and yield, but using excessive amount of PP/4CSP led to over-oxidation to form geranic acid and 6-methyl-5-hepten-2-one. Finally, the appropriate molar ratio of geraniol and PP/4CSP selected and used for further experiments is 3:10. In the next series of experiments, power of microwave irradiation as well as reaction time were investigated to find out the most efficient reaction conditions (Entry 6-11, Table 1). The results showed that geranial formed from

the oxidation of geraniol by using PP/4CSP was obtained in good yield (67%) under fourteen-minute microwave irradiation.

Table 1. The reaction factors influenced on the oxidation of geraniol by **PP/4CSP** in solvent-free media.[a]



(**1a**) (**3a**)

Entry	Geraniol (mmol)	$KMnO_4$ (mmol)	$CuSO_4 \cdot 5H_2O$ (mmol)	Power (Temp)[b] W (^oC)	Time (min)	Yield[c] (**3a**) (%)
1	3	2	8	45 (84)	10	15
2	3	4	16	45 (84)	10	21
3	3	6	24	45 (88)	10	31
4	3	8	32	45 (90)	10	44
5	3	10	40	45 (90)	10	51
6	3	12	48	45 (94)	10	46
7	3	10	40	30 (78)	10	33
8	3	10	40	60 (110)	10	38
9	3	10	40	45 (90)	12	53
10	3	10	40	45 (94)	14	67
11	3	10	40	45 (100)	16	64
12[d]	3	10	40	94	10	42
13[d]	3	10	40	94	20	60
14[d]	3	10	40	94	30	51

[a] The reactions were performed under microwave irradiation.

[b] Temp. = the temperature of the reaction mixture was measured by thermometer immediately after the stop of the reaction.

[c] Yields were calculated based on GC-FID analyses.

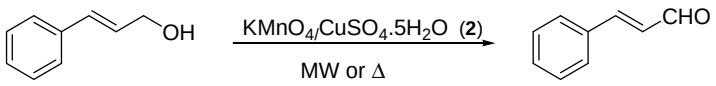
[d] The reactions were performed under conventional heating.

3.2. Oxidation of cinnamyl alcohol into cinnamaldehyde.

Based on the achievement of the oxidation of geraniol, we continued to select cinnamyl alcohol, a natural unsaturated alcohol as model substrate. Similarly, the molar ratio of cinnamyl alcohol and PP/4CSP were investigated at 60 W for 10 minutes under microwave irradiation (Entry 1-5, Table 2) in detail in order to find out the good molar ratios. The results showed that using excessive amount of PP/4CSP led to reducing yield of cinnamaldehyde. The main reasons are explained that excessive amount of PP/4CSP oxidized directly a new-born cinnamaldehyde into cinnamic acid under microwave irradiation. Further experiments on power of microwave oven and reaction time as in Entry 7-11, Table 2 showed that cinnamaldehyde formed from the

oxidation of cinnamyl alcohol by using PP/4CSP was obtained in good yield (61%) under twelve-minute microwave irradiation.

Table 2. The reaction factors influenced on the oxidation of cinnamyl alcohol by **PP/4CSP** in solvent-free media.[a]



(**1b**) (**3b**)

Entry	Cinnamyl alcohol (mmol)	$KMnO_4$ (mmol)	$CuSO_4 \cdot 5H_2O$ (mmol)	Power (Temp)[b] W (^oC)	Time (min)	Yield[c] (**3b**) (%)
1	3	2	8	60 (86)	10	40
2	3	4	14	60 (90)	10	45
3	3	6	24	60 (90)	10	49
4	3	8	32	60 (92)	10	41
5	3	10	40	60 (96)	10	21
6	3	6	24	45 (84)	10	29
7	3	6	24	75 (92)	10	59
8	3	6	24	90 (98)	10	54
9	3	6	24	75 (90)	8	41
10	3	6	24	75 (94)	12	61
11	3	6	24	75 (96)	14	51
12[d]	3	6	24	94	10	60
13[d]	3	6	24	94	12	62
14[d]	3	6	24	94	20	59

[a] The reactions were performed under microwave irradiation.

[b] Temp. = the temperature of the reaction mixture was measured by thermometer immediately after the stop of the reaction.

[c] Yields were calculated based on GC-FID analyses.

[d] The reactions were performed under conventional heating.

Microwave irradiation inevitably affects a rise of the reaction temperature of the reaction mixture, and it would therefore be of interest to check whether the drastically shortened reaction times could be affected simply by the higher reaction temperatures. Thus a series of experiments were performed under conventional heating at the same reaction temperature, same reaction time with those under microwave irradiation or at various reaction time to get higher yield for both oxidation of geraniol (Entry 12-14, Table 1) and cinnamyl alcohol (Entry 12-14, Table 2). The summary results of two activation methods represented in Table 3 showed that these conversions were easily occurred at high temperature, but with internal heating, microwave irradiation

influenced efficiently on reaching high temperature in shorter time than conventional heating did.

Table 3. Summary results of the oxidation of geraniol and cinnamyl alcohols by **PP/4CSP** under solvent-free condition.

Alcohols	Molar ratio of alcohol : PP/4CSP	Yield % (Time, Temperature)	
		Microwave	Conventional heating
Geraniol	3:10:40	67 (14 min, 94^{o}C)	60 (20 min, 94^{o}C)
Cinnamyl alcohol	3:6:24	61 (12 min, 94^{o}C)	62 (12 min, 94^{o}C)

In the next step, a comparison table of our work with the previous literature on the oxidation of geraniol illustrated that besides the yield of geranial obtained in our work was slightly higher than those in the previous literature, PP/4CSP is also regarded as a green and inexpensive oxidant, and used for solvent-free oxidation reactions, especially assisted by microwave irradiation in order to reduce the cost of operation and get better yields in short time (Table 4). While tetrapropylammonium perruthenate (TPAP) as oxidant combined with *N*-methylmorpholine *N*-oxide (NMO) used for oxidation of geraniol were not stable, *e.g.* NMO is hygroscopic, and TPAP can explode when heated; besides dichloromethane and acetonitrile as reaction solvents are toxic and hazardous in case of eye contact, inhalation or ingestion [8]. In addition, using oxygen molecule or hydrogen peroxide are usually appreciated highly based on the principles of green chemistry, however these oxidation reactions must be performed in the special instrument being able to resist high pressure [10, 11], or promoted by expensive and non-commercially available catalysts [11,13].

Table 4. Comparison table of previous literatures on the oxidation of geraniol and cinnamyl alcohol.

Oxidant	Geraniol	Cinnamyl alcohol
PP/4CSP, solvent-free, MW	67 % (14 min, 94 ^{o}C)	61 (12 min, 94 ^{o}C)
TPAP, NMO, CH_2Cl_2, CH_3CN	65 % (20 - 45 min., r.t.) [8]	-
O_2/$scCO_2$, 5 wt% Pd/Silica mixed with 0.2 g silica	59 % (3 - 4 hrs, 80 ^{o}C) [10]	-
O_2/$scCO_2$ with CrMCM-41	52 % (6 hrs, 80 ^{o}C) [11]	-
H_2O_2 with WO_3-SiO_2-700	63 % (2 hrs, 70 ^{o}C) [13]	-

4. CONCLUSIONS

Comprehensive experimental work has made it possible for us to introduce a selective, efficient and solvent-free oxidation of geraniol and cinnamyl alcohol into valuable saturated aldehydes by PP/4CSP. Furthermore, solid potassium permanganate used is less skin irritant than its solution (safe for use), easy to operate the procedure, and specially generates desired products with good yields in short time under the assistance of microwave irradiation at 94 ^{o}C, *e.g.* max. 67 % of geranial and max. 61 % of cinnamaldehyde. In order to increase oxidative ability of solid potassium permanganate, the amount of $KMnO_4$ was used much more than

equivalent molar amount of alcohols, moreover copper(II) sulfate pentahydrate was necessary to promote the oxidative ability of solid potassium permanganate.

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TÓM TẮT

SỰ OXID HÓA CHỌN LỌC VÀ HIỆU QUẢ TRÊN CÁC ALCOL BẤT BÃO HÒA LÀ CÁC CẤU TỬ CHÍNH TRONG TINH DẦU

Lưu Thị Xuân Thi

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Alcol bất bão hòa có trong tinh dầu được oxid hóa rất hiệu quả thành các aldehyd bất bão hòa tương ứng bằng permanganat kali tẩm trên sulfat đồng (II) ngậm năm phân tử nước. Các aldehyde bất bão hòa như geranial và cinnamaldehyd là các hợp chất có giá trị trong thực phẩm, mỹ phẩm, hương liệu và hóa dược được tạo thành với hiệu suất khá cao (> 60 %) dưới hai phương pháp kích hoạt: chiếu xạ vi sóng và đun nóng cổ điển.

Từ khóa: potassium permanganate, copper (II) sulfate, microwave irradiation, unsaturated alcohol.