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LEUCINE : AN EFFICIENT AND GREEN AMINO ACID CATALYST FOR CONVERSION OF ALDEHYDES AND KETONES INTO GEM-DIHYDROPEROXIDES WITH H_2O_2

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ABSTRACT

Leucine amino acid, has been explored as an effective catalyst for conversion of ketones and aldehydes into corresponding *gem*-dihydroperoxides using 30% aqueous hydrogen peroxide in acetonitrile at room temperature. The reactions proceed smoothly within short periods of time to provide the respective *gem*-dihydroperoxides in excellent yields. Mild reaction conditions, low reaction times, high yields, low environmental impact, use of non-expensive, recyclable and green catalyst are the main merits of the present method.

Keywords

Gem-dihydroperoxide; leucine; amino acid; hydrogen peroxide; aldehyde; ketone

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1. INTRODUCTION

Gem-dihydroperoxides (DHPs) are considered as stable derivatives of ketones and aldehydes [1], which have been of considerable interest because of their relevance to peroxidic antimalarial drugs [2]. Also, these compounds are important intermediates in the synthesis of a number of classes of peroxides including tetraoxanes [3], silateraoxans [4], spirobisperoxyketals [5], bisperoxyketals [6], and 1,2,4,5-tetraoxacycloalkanes [7]. *Gem*-dihydroperoxides have also been employed as initiators for radical polymerization reactions [8], as precursors for synthesis of dicarboxylic acid esters [9], and as reagents for oxidation reactions such epoxidation of α,β-unsaturated ketones [10], enantioselective oxidation of 2-substituted 1,4-naphtoquinones [11], oxidation of sulfides [12], and as suitable oxidants in other synthetic organic reactions [27]. Three major methods reported for the synthesis of *gem*-dihydroperoxides are: (i) ozonolysis of ketone eneol ethers or α-olefines in the presence of aqueous H_2O_2 [7a, 13], (ii) reaction of ketals with H_2O_2 in the presence of tungstic acid [14], or $BF_3.Et_2O$ [15] and (iv) peroxidation of ketones using an acidic solvent [16]. However, many of these methods have certain drawbacks including the use of concentrated H_2O_2 and excess acid, low yield, limited substrate range and production of mixtures of peroxidic products [17]. Also, poor selectivity and the presence of ozone sensitive groups in the substrates are further limitations in ozonolysis reaction. In order to avoid such limitations, recently, reactions of ketones and aldehydes with H_2O_2 in the presence of Lewis acids in organic solvents have been reported. Amongst the Lewis acids, I_2 [18], ceric ammonium nitrate (CAN) [19], CSA [20], $NaHSO_4.SiO_2$ [21], Re_2O_7 [22] and PMA [23] have been reported as the catalysts in the synthesis of *gem*-dihydroperoxides with aqueous H_2O_2. With respect to the increasing concern on the environmental issue and also to comply with the principles of the green chemistry [24], we are encouraged in the present research to examine the catalytic efficiency of leucine amino acid as a green and inexpensive catalyst for the synthesis of *gem*-dihydroperoxides from aldehydes and ketones using hydrogen peroxide. It is important to note that, so far no report on the use of amino acids as catalysts in the synthesis of *gem*-dihydroperoxides from aldehydes and ketones has appeared in the literature.

2. EXPERIMENTAL

2.1 Material and instruments

Solvents and chemicals were obtained from Aldrich and Merck chemical companies and used without purification. Melting points were determined in open capillary tubes in a Stuart SMP_3 apparatus and uncorrected. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrometer at 90 and 22.5 MHz respectively using Me_4Si as an internal standard. IR spectra were recorded on a Perkin Elmer GX FT IR spectrometer (KBr pellets).

Caution: Although we did not encounter any problem with these reactions, peroxidic compounds are potentially explosive and should be handled with precautions; all reactions should be carried out behind a safety shield inside a fume hood and transition metal salts or heating should be avoided.

2.2 General procedure for conversion of ketones and aldehydes into corresponding *gem*-dihydroperoxides

To a mixture of carbonyl compound **1** (1 mmol), and leucine (14 mg, 0.1 mmol) in MeCN (4 mL) was added 30% aqueous H_2O_2 (2 mL), and the mixture was stirred at room temperature for an appropriate time (Table 2). After completion of the reaction as monitored by TLC, the product was extracted with chloroform (3×4 mL). Then, the combined organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by silica-packed column chromatography (hexane-EtOAc) to afford pure *gem*-dihydroperoxides (Table 2). The products were characterized on the basis of their physical and spectral (^1H, ^{13}C NMR and IR) data and compared with those reported in the literature (Table 2). The characteristic data for some representative and new products are given below.

Methyl-(naphthalen-1-yl)-1,1-dihydroperoxide (2k). Colorless oil; IR (KBr), v: 3324, 3052 (O-H stretching), 2922, 2853, 1594, 1573, 1508, 1461, 1356, 1279, 1240, 1192, 1128, 941, 863, 802, 775, 591 cm^{-1}; MS (FABMS, 70 ev): m/z (%): 243 $(M+Na)^+$; ^1H-NMR ($CDCl_3$, 90 MHz): δ 8.83-8.75 (brs, 2H, OOH), 8.10-7.20 (m, 7H, Ar-H), 2.66 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 136.0, 134.4, 131.1, 129.9, 127.8, 126.6, 125.5, 123.0, 107.0, 20.5; *Anal*. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45%. Found: C, 65.42; H, 5.40%.

(4-Bromophenyl)methylene-1,1-dihydroperoxide (2t). Colorless solid; mp 88-90 °C; IR (KBr), v: 3426, 3085 (O-H stretching), 2909, 1608, 1528, 1411, 1353, 1236, 1195, 1083, 973, 856, 828, 753, 706, 601 cm^{-1}; MS (FABMS, 70 ev): m/z (%): 258 $(M+Na)^+$; ^1H-NMR ($CDCl_3$, 90 MHz): δ 9.96 (brs, 2H, OOH), 7.90-7.00 (m, 4H, Ar-H), 6.26 (s, 1H, CH); ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 141.0, 132.5, 130.5, 120.0, 111.0; *Anal*. Calcd for $C_7H_7BrO_4$: C, 35.74; H, 2.97%. Found: C, 35.72; H, 2.94%.

(4-Flourophenyl)methylene-1,1-dihydroperoxide (2u). Colorless solid; mp 110-112 °C; IR (KBr), v: 3464, 3082 (O-H stretching), 2905, 1625, 1601, 1564, 1453, 1353, 1303, 1071, 1025, 844, 720, 685 cm^{-1}; MS (FABMS, 70 ev): m/z (%): 197 $(M+Na)^+$; ^1H-NMR ($CDCl_3$, 90 MHz): δ 9.21 (brs, 2H, OOH), 8.14-7.14 (m, 4H, Ar-H), 6.14 (s, 1H, CH); ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 161.62, 137.0, 128.5, 118.5, 112.0; *Anal*. Calcd for $C_7H_7FO_4$: C, 48.27; H, 4.02%. Found: C, 48.23; H, 3.97%.

(2-Methoxyphenyl)methylene-1,1-dihydroperoxide (2v). Colorless oil; IR (KBr), v: 3226, 3085 (O-H stretching), 2853, 1647, 1603, 1493, 1465, 1372, 1245, 1177, 1017, 844, 758 cm^{-1}; MS (FABMS, 70 ev): m/z (%): 209 $(M+Na)^+$; ^1H-NMR ($CDCl_3$, 90 MHz): δ 9.35 (brs, 2H, OOH), 8.18-6.84 (m, 4H, Ar-H), 6.04 (s, 1H, CH), 4.05 (s, 3H, OCH_3); ^{13}C-NMR ($CDCl_3$,

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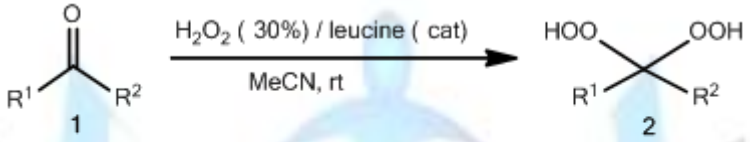
22.5 MHz): δ 157.4, 139.1, 128.5, 123.0, 118.5, 102.0, 57.5; *Anal*. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.37%. Found: C, 51.57; H, 5.34%.

(Pyridin-3-yl)methylene-1,1-dihydroperoxide (2x). Colorless solid; Mp. > 160 °C; IR (KBr), v: 3410, 2941, 1635, 1450, 1393, 1139, 996, 640, 521 cm^{-1}; ^{1}H-NMR (d_6-DMSO, 90 MHz): δ 9.75 (brs, 2H, OOH), 8.71-7.23 (m, 4H, Ar-H), 7.18 (s, 1H, CH); ^{13}C-NMR ($CDCl_3$, 22.5 MHz): δ 150.9, 142.1, 137.6, 124.4, 118.2, 53.8; *Anal*. Calcd for $C_6H_7NO_4$: C, 45.86; H, 4.46; N, 8.91%. Found: C, 45.48; H, 4.42; N, 8.65%.

(Quinolin-2-yl)methylene-1,1-dihydroperoxide (2y). Yello solid; Mp. 138-140 °C; IR (KBr), v: 3425, 3250, 2958, 1660, 1629, 1600, 1375, 1355, 1111, 807, 779, 636 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 8.95 (brs, 2H, OOH), 7.49-8.25 (m, 6H, Ar-H), 6.61 (s, 1H, CH); *Anal*. Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.35; N, 6.76%. Found: C, 57.82; H, 4.32; N, 6.73%.

3. RESULTS AND DISCUSSION

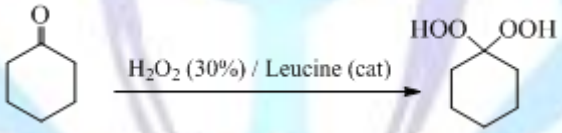
In continuation of our efforts to explore new and benign catalysts for the synthesis of *gem*-dihydroperoxides [25], and their applications as versatile and high potent oxidants in various organic transformations [26], herein, we wish to introduce the leucine amino acid as a cheap, green and effective catalyst in the synthesis of *gem*-dihydroperoxides from ketones and aldehydes with 30% aqueous H_2O_2 at room temperature (scheme 1).



Scheme 1. Leucine-catalyzed oxidative conversion of aldehydes and ketones to *gem*-dihydroperoxides with H_2O_2 (30 %).

In an effort to establish the reaction conditions, various reaction parameters were studied for the preparation of 1,1-dihydroperoxycyclohexane through the model reaction of cyclohexanone with 30 % aqueous H_2O_2 under the catalytic effect of leucine using different solvents such as CH_2Cl_2, Et_2O, AcOEt, CH_3CN and the results are summarized in Table 1. As seen in this Table, the best result in terms of yield and reaction time was obtained using MeCN as the solvent of choice and 10 mol% catalyst loading at room temperature (entry 5). The importance of the catalyst in this reaction was verified by conductiong the reaction in the absence of leucine that resulted in trace amount of the product (entry 10).

Table 1. Screening the reaction parameters for the formation of 1,1-dihydroperoxycyclohexane[a]



Entry	Solvent	Leucine (mol%)	Temperature (°C)	Time (min)	Yield[b] (%)
1	CH_2Cl_2	10	rt	60	70
2	Et_2O	10	rt	120	58
3	AcOEt	10	rt	70	87
4	EtOH	10	rt	80	85
5	CH_3CN	10	rt	20	96
6	CH_3CN	5	rt	30	75
7	CH_3CN	20	rt	20	92
8	CH_3CN	10	40	60	68
9	CH_3CN	10	60	60	65
10	CH_3CN	No catalyst	rt	120	trace

[a] Conditiones: cyclohexanone (1 mmol), 30 % aqueous H_2O_2 (3 mL), solvent (4 mL).

[b] Isolated yield.

With optimized conditions in hand (aq. 30% H_2O_2, 10 mol% catalyst, MeCN, rt) we began to study the scope of the reaction using a range of aliphatic and aromatic aldehydes and ketones as summarized in Table 2. As shown in Table 2,

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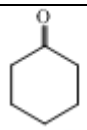
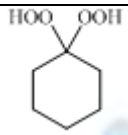
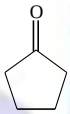
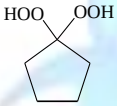
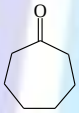
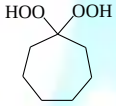
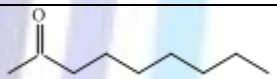
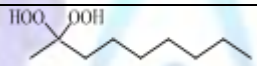
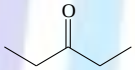
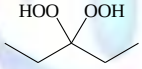
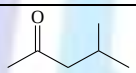
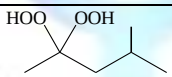
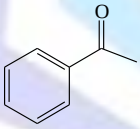
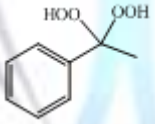
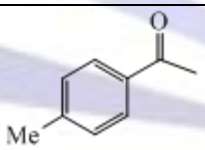
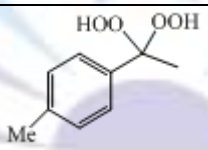
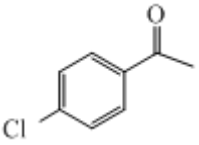
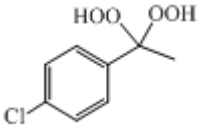
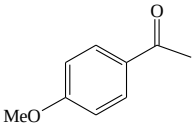
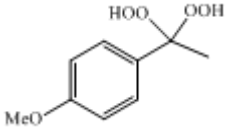
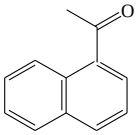
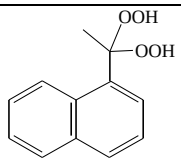
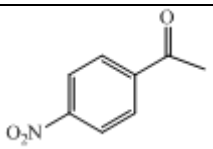
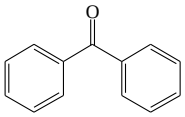
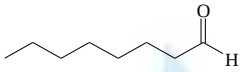
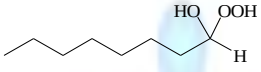
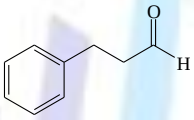
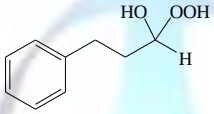
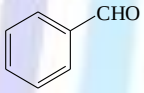
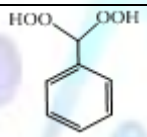
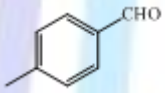
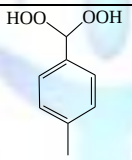
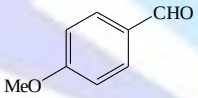
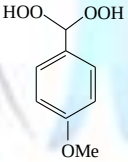
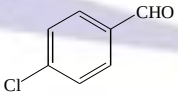
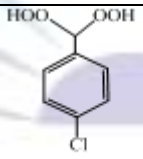
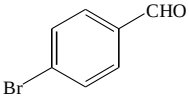
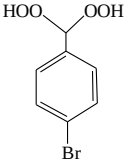
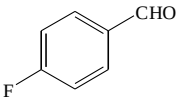
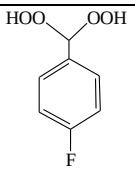
the aliphatic ketones **1a-f** generally react faster than the aromatic ones **1g-k** to afford the corresponding *gem*-dihydroperoxides comparatively in higher yields. Similarly, the aromatic aldehydes **1p-y** were quantitatively converted to the corresponding DHPs with relatively longer reaction times. However, this procedure proved to be unsuitable for the preparation of DHPs from the aromatic ketones **1l** and **1m** which remained untouched after *ca* 3 h reaction under the optimized conditions. This can be possibly explained by the strong resonance stabilization effects on the carbonyl group. It was interesting to note that, the addition of only one molecule of hydrogen peroxide to the carbonyl group occurs in reactions of aliphatic aldehydes such as **1n** and **1o** to result in the formation of 1,1-hydroxyhydroperoxide derivatives instead of the expected DHPs compounds.

Table 2. Leucine-catalyzed conversion of aldehydes and ketones into *gem*-dihydroperoxides with 30% aq. H_2O_2[a]

Entry	Ketone & Aldehyde **1**	Product[b] **2**	Time (min)	Yield (%)[c]	Mp (°C)	Ref.
a			20	96	oil	[20]
b			15	98	oil	[23a]
c			13	97	62-64	[22]
d			15	98	oil	[18a]
e			20	92	oil	[19]
f			18	95	oil	[19]
g			180	80	76-78	[19]
h			250	65	oil	[26h]
i			150	80	oil	[26h]
j			290	65	oil	[18b]

k			140	85	oil	[25d]
l		–	300	–	–	–
m		–	300	–	–	[25d]
n			50	95	oil	[27]
o			80	96	oil	[28]
p			30	85	oil	[19]
q			65	90	56-58	[18a]
r			100	80	oil	[23a]
s			50	92	74-76	[18a]
t			65	90	86-88	[25d]
u			35	86	112-114	[25d]

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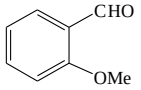
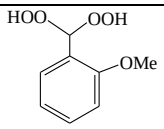
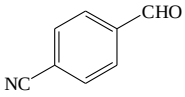
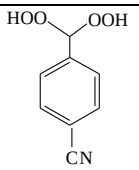
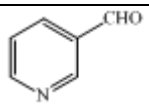
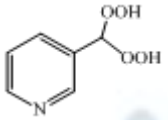
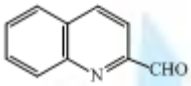
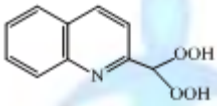
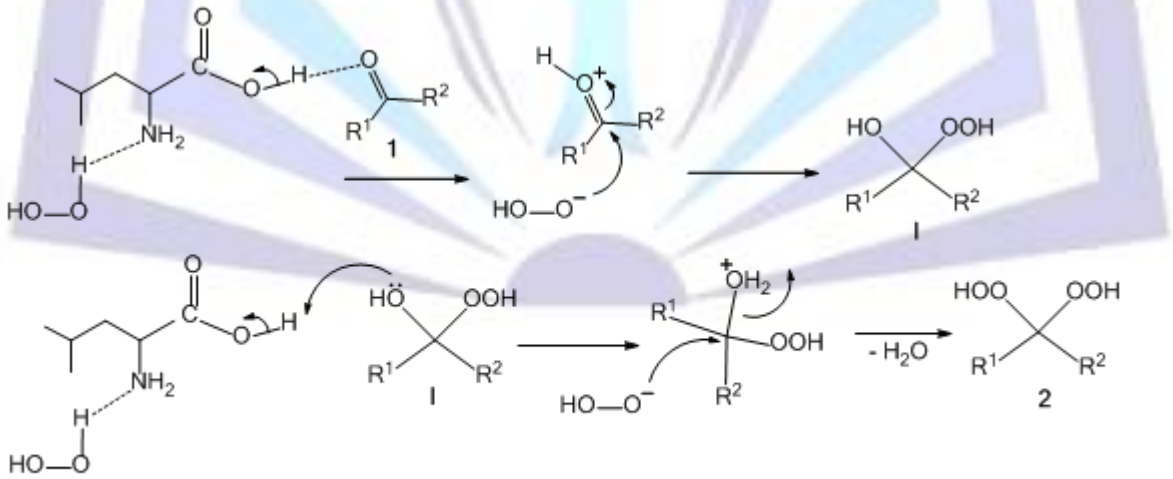
v			120	70	oil	[25d]
w			80	75	106-108	[25a]
x[new]			20	76	> 160	-
y[new]			30	88	138-140	-

[a] Conditions: ketone and aldehyde (1 mmol), CH_3CN (4 mL), leucine (13 mg, 0.1 mmol), 30% aq. H_2O_2 (3 mL), reactions are carried out at rt.

[b] The structures of the products were established from their physical properties and spectral (^{1}H NMR, ^{13}C NMR and IR) analysis and compared with the data reported in the literature.

[c] Isolated Yield.

A reasonable mechanism to explain the conversion of ketones and aldehydes **1** into respective *gem*-DHPs **2** is given in Scheme 2. As shown in this Scheme, the initial step likely involves the activation of carbonyl compound **1** through protonation with leucine carboxyl group. Then, the protonated carbonyl undergoes nucleophilic addition with deprotonated hydrogen peroxide to produce the adduct **I**. Subsequently, the resulting hydroxyl group in the intermediate **I** is protonated by leucine carboxyl group followed by nucleophilic substitution with a second molecule of hydrogen peroxide anion to furnish the product **2**.



Scheme 2. Leucine-catalyzed synthesis of *gem*-dihydroperoxides from ketones and aldehydes.

CONCLUSIONS

In summary, Leucine amino acid has been explored as an efficient, reusable and green catalyst which can effectively accelerate the conversion of ketones and aldehydes into their corresponding *gem*-dihydroperoxides. These reactions proceed smoothly with low reaction times at room temperature to furnish the titled products in high to excellent yields.

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