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Novel mild synthesis of high-added-value *p*-hydroxyphenyl acetic acid and 3,4-dihydroxyphenyl acetic acid using the acidic clay/hydrogen peroxide catalytic system

Soumaya Bouguerra Neji ^a, Samia Azabou ^b, Sandra Contreras ^c,
Francisco Medina ^c, Mohamed Bouaziz ^{d,*}^a Laboratoire de Chimie appliquée Hétérocycle Corps Gras Polymères Faculté des Sciences de Sfax, 3038, Université de Sfax, Tunisia^b Laboratoire Analyse Valorisation et Sécurité des Aliments, Ecole Nationale d'Ingénieurs de Sfax, 3038 Sfax, Tunisia^c Departament d'Enginyeria Química, Universitat Rovira i Virgili, Campus Sescelades, 43007 Tarragona, Spain^d Laboratoire d'Electrochimie et Environnement, Ecole Nationale d'Ingénieur de Sfax, BP 1173, 3038 Sfax, Université de Sfax, Tunisia

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ABSTRACT

Acid-activated clays KSF and KSF/O were successfully used in the hydrogen peroxide conversion of phenyl acetic acid to high-added phenolic compounds: *p*-hydroxyphenyl acetic acid and 3,4-dihydroxyphenyl acetic acid, endowed with a powerful antioxidant capacity. The catalytic conversion enhancement could be correlated to the total surface acidity and the high iron content of the catalysts KSF/O and KSF, respectively. The synthetic route described here was conducted under mild conditions with very low degree of mineralization and without significant Fe ion leaching observations. The synthesis reaction is operationally simple and could find application for industrial purposes.

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1. Introduction

There is a growing interest in natural and unnatural antioxidants as a protective strategy against various diseases such as atherosclerosis, ischemia-reperfusion injury and inflammatory injury by blockage or removal of oxidative stresses [1]. Ascorbic acid, vitamin E and polyphenols are the major antioxidants used as dietary supplements for the prevention of such diseases. Phenolic compounds have many industrial applications as natural additives with antimicrobial and/or antioxidant properties that are important in protecting the nutritive value and increasing the shelf life of cosmetic and food products. In addition, they are considered as one of the bioactive compound groups which are responsible for beneficial health effects

[2,3]. From a chemical point of view, phenolic compounds can be classified in different ways because they are constituted by a large number of heterogeneous structures that range from simple molecules to highly polymerized compounds [4]. The antioxidant activity of phenolic compounds depends largely on the chemical structure of these substances [5] with flavonoids, tannins, chalcones and coumarins as well as phenolic acids, being the most highlighted ones. For instance, antioxidant activity of phenolic acids, especially hydroxycinnamic acids and hydroxybenzoic acids, is usually determined by the number of hydroxyl groups found in the molecule thereof [6].

Although a great amount of phenolic compounds can be found in plants, it could be very interesting to easily synthesize them with competitive prices, so that industrial investigation of their biological properties can occur more frequently. Accordingly, many different routes were published for total synthesis of phenolic antioxidant compounds. Among useful transformations, hydroxylation of

* Corresponding author.

E-mail address: mohamed.bouaziz@fsg.rnu.tn (M. Bouaziz).

aromatic compounds stands out as a fundamental reaction due to its many uses in the manufacture of high-added-value compounds, like orthodiphenol compounds such as hydroxytyrosol (3,4-dihydroxyphenylethanol) and 3,4-dihydroxyphenyl acetic acid [7].

In the course of the development of an efficient synthetic route of a potent antioxidant, we can describe herein a new alternative method of a two-step-synthesis of 3,4-dihydroxyphenyl acetic acid using the advanced oxidation of phenyl acetic acid under mild conditions. Actually, this synthetic route is based on literature analogies used for the synthesis of hydroxytyrosol [8]. Though the difference with the latter is the use of acid-activated clay instead of (Al–Fe) pillared one without ultra-violet light. As a matter of fact, acid-activated clays are one of the most widely studied solid acid catalysts for many organic transformations due to their environmental compatibility, low cost, high selectivity and thermal stability [9].

2. Materials and methods

2.1. Reagents

Phenylacetic acid (PAA) was obtained from Sigma-Aldrich (St. Louis, MO). *para*-hydroxyphenyl acetic (*p*-HPAA) acid and 3,4-dihydroxyphenyl acetic (3,4-DHPAA) used as standards for chromatographic calibration were also purchased from Sigma-Aldrich. Hydrogen peroxide (30% solution in water) was obtained from CePharma (Tunisia). Deionized water was used throughout the experiments and in the HPLC mobile phase. Pure HPLC solvents were used in all cases.

2.2. Catalysts

The commercial clays (Montmorillonite KSF/0 clay, Montmorillonite KSF clay and Montmorillonite K10 clay) used as catalysts in this study were purchased from Fluka and used without further treatment. In fact, the relevant physico-chemical properties of the catalysts used are given in Table 1 [10]. The total acidity of the catalysts was determined by NH₃ adsorption. Following a 2 h pretreatment at 300 °C, NH₃ was adsorbed at ambient temperature. After evacuating, the amount of the chemisorbed NH₃ was measured applying 2 °C/min heating rate till 500 °C.

2.3. Phenyl acetic acid conversion

Phenylacetic acid oxidation was carried out in a 100 ml Pyrex reactor equipped with a magnetic stirrer. The solid

catalyst was introduced into 50 mL of PAA aqueous solution (500 mg L⁻¹), under continuous stirring. The desired quantity of H₂O₂ (0.02 M) was added indicating the start of the reaction. During the experiments, aliquots were withdrawn at regular intervals with the purpose of monitoring the conversion of PAA to *p*-HPAA and then to 3,4-DHPAA after being immediately filtered to completely remove catalyst particles.

2.4. HPLC analysis

Monomeric phenols (PAA, *p*-HPAA and 3,4-DHPAA) were analysed on a high performance liquid chromatograph (Dionex HPLC) equipped with a C18 column (4.6 mm × 250 mm; Shimpack VPODS).

2.5. LC–MS/MS analysis

LC-UV-MS/MS analyses were performed as described by Kite et al. [11] on a Thermo Scientific System consisting of an Accela U-HPLC unit with a photodiode array detector and an LTQ Orbitrap XL mass spectrometer fitted with an electrospray source. Chromatography was performed with 5 µl sample injections onto a 150 × 3 mm i.d., 3 µm, Luna C18(2) column (Phenomenex) using a 400 µl/min linear mobile phase with a methanol/water/acetonitrile + 1% gradient. Formic acid changes from 0:90:10 to 90:0:10 over 20 min followed by an isocratic phase for 5 min afterwards, a column washing phase for equilibrium per-pauses was performed during 3 min before the next injection. The ESI source of the mass spectrometer was operated in both positive and negative modes under the recommended manufacturers' conditions for the mobile phase parameters. An orbitrap mass analyser was set to scan in a range of *m/z* 200–2000 at 30,000 resolutions in one polarity, while the linear ion-trap analysis was performed. Analyses of MS were due on the most abundant ions in both polarities using an ion isolated window of +2 *m/z* and relative collision energy of 35%. For accurate mass analyses of product ions generated by MS2 in the ion trap, were scanned by the orbitrap at 7000 resolutions. Negative mode ESI was used since the phenolic compounds in question ionize better in this mode, as described by other authors about these species [12]. Acidification of the LC mobile phase allows the best separation, since the hydroxyl groups in the compounds are kept in their acidic form, thereby increasing their retention on the column and decreasing peak broadening.

Table 1

Some characteristic data of the investigated catalysts.

Catalyst	Textural characteristics		Analysis (%)		Acidity		
	Specific surface area (m ² /g)	Average pore diameter (Å)	Al	Fe	pH	IR spectra (AU)	
						Brønsted	Lewis
KSF/0	117	74	6.16	1.37	1.3	1.03	0.20
KSF	30	50	8.62	3.17	1.5	0.59	0.15
K10	249	56	7.71	1.99	4.5	0.33	0.29

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