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RESEARCH ARTICLE

HIGHLY EFFICIENT ESTERIFICATION OF PHENOLIC ACID OVER METAL EXCHANGED MONTMORILLONITE CLAY

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ABSTRACT

A simple and efficient method for the preparation of polyphenolic esters catalysed by various metal exchanged montmorillonites in an enviro-economic route is reported. The activity of the catalysts follows the sequence: $Fe^{3+}>Zn^{2+}>Cu^{2+}>Al^{3+}$-mont>K-10- montmorillonite.

Keywords: esterification, polyphenols, K-10- montmorillonite.

Graphical Abstract

$$nArCOOH + R(OH)_n \xrightarrow[\text{Reflux}]{\text{Catalyst, } CHCl_3} (ArCOO)_nR$$

ArCOOH = Phenolic acid
Catalyst = various metal exchanged montmorillonites showing the activity order : $Fe^{3+}>Zn^{2+}>Cu^{2+}>Al^{3+}$-mont> K-10- mont

INTRODUCTION

Polyphenols are generally defined as a diverse group of naturally occurring compounds containing multiple phenolic functionalities which are commonly found in higher plants (Handique and Baruah, 2002). Tremendous growth in research of polyphenols has been noticed because many of them exhibit a broad spectrum of biological activities along with antioxidant activities (Haslam, 1998, Kono, *et al.*, 1997, Hsu, *et al.*, 2005, Lee *et al.*, 2005, Chen and Ho, 1997). Polyphenolic esters are potential antioxidants with multiple mechanisms involving free radical scavenging, metal ion chelation and inhibitory action on specific enzymes that induce free radical and lipid hydroperoxide formation (Son and Lewis, 2002). Polygalloyl dendrimers are reported to serve as potential leads for the development of new topical drugs to be used in burn wound treatment (Halkes, *et al.*, 2002). Phenolic acid ester motifs have been found in bioactive natural products, for example, the NF-κB inhibitors CAPE (Natarajan, *et al.*, 1996) and capsiate (Sancho *et al.*, 2002), honeybee propolis contact allergen prenyl caffeate (Stüwe *et al.*, 1989), and the EGCG mimic and HIV-1 reverse

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transcriptase inhibitor hydroxyl tyrosol gallate (Tillekeratne *et al.,* 2001). In many cases phenolic acid esters are also used as important intermediates for the medicine synthesis (Rotella, *et al.*, 2000, Xu, *et al.,* 2002).

Despite the current excitement for the potential beneficial effects of polyphenols on human health, there is still a great shortage of methods for the chemical modification and synthesis of these compounds, that generally occur as complex mixtures of analogues/homologues and therefore difficult to obtain in pure form by isolation. Although these compounds are structurally unsophisticated, their reported synthesis typically suffer from a heavy burden of protecting groups for the purpose of improved chemoselectivity (Natarajan, *et al.,* 1996, Sancho *et al.,* 2002, Stüwe *et al.,* 1989, Tillekeratne, et al 2001, Rotella, *et al.,* 2000, Xu, *et al.,* 2002). One of the most desired synthetic requirements in polyphenol chemistry is the efficient esterification of phenolic acids, since the ester moiety is widespread in dietary polyphenolics. In the presence of strong protic acids (Fisher esterification) phenolic acids could be esterified with good chemoselectivity (Burke *et al.,* 1995), but harsh reaction conditions made that strategy of limited applicability. In connection with our research program directed toward the synthesis of polyphenols with potential antioxidant activities, we report here a novel and highly efficient protocol for esterification of equivalent amount of phenolic acids with poly hydroxyl compounds mediated by metal exchanged montmorillonite clay as a strong solid acid catalyst which fulfils our interest of green chemical synthesis. Our protocol has the following advantages over other direct esterification catalyst systems- (i) high catalytic activity, (ii) simple work up procedure and (iii) nonpolluting and reusable catalyst.

Montmorillonites can be structurally defined as layers of negatively charged two dimensional silicate sheets that are separated by interlayer cationic species with high exchange ability for other metal polycations (Clark and Macquarrie, 1996, Laszlo, 1986, Pinnavaia, 1983). In recent years, both natural and cation exchanged form of montmorillonites emerge as efficient solid acid catalysts in various organic transformations owing their Bronsted and Lewis acidities (Joseph, *et al.,* 2005, Srinivas and Das, 2003, Kawabata, *et al.,* 2001, Kawabata, *et al.,* 2003, Bandgar, *et al.,* 2001, Li, *et al.,* 1997). We have introduced Fe^{3+}, Zn^{2+}, Cu^{2+} and Al^{3+} cationic species within the interlayers of montmorillonite with an aim to develop a strong and efficient procedure for the direct esterification of phenolic acids with polyhydroxy compounds.

MATERIALS AND METHODS

The IR spectra were determined as KBr pellets on Shimadzu model IR Prestige 21 spectrophotometer (FTIR). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Varian FT spectrometer in DMSO-d_6 with tetramethylsilane as internal standard. Mass spectra were recorded on JEOL mass spectrometer. Elemental analyses were performed by Elementar Vario EL III/Carlo Erba 1108.

Preparation of the catalyst

K-10- mont was purchased from Fluka Chemicals. The clay has the following chemical compositions (main elements) SiO_2, 67.6; Al_2O_3, 14.6; Fe_2O_3, 2.9; MgO, 1.8. The characteristics of K-10- mont are (1) surface area = 220-270m^2/g, (2) bulk density = 300-370g/l, (3) specific gravity = 2.5g/ml, (4) refractive index = 1.51 and (5) crystal system, monoclinic.

Metal exchanged mont is prepared according to known procedure (Laszlo and Mathy, 1987). To 1L of 1M aqueous metal chloride solution, 80g of K-10- mont was added. Stirring was done for 24-30 hrs in order to saturate the exchange capacity of K-10- mont. The clay suspension was centrifused and the supernatant solution was discarded. The clay catalyst was washed each time with fresh distilled water until free of chloride ions as confirmed by $AgNO_3$ test. The catalyst was dried overnight in an oven at 120°C and finely ground in a mortar.

Characterization of the catalysts

Powder X-ray diffraction patterns of the clay catalysts were recorded after drying at 110°C to

confirm their layered structures. The XRD patterns were recorded using a Rigaku miniflex X-ray diffractogram, set up with Cu Kα radiation and a graphite monochromatic with scan speed 3° min^{-1} and scanning in the 2θ range from 10 to 80 2θ. The interlayer spaces were estimated to be 2.2, 4.2, 2.6, 3.4 and 2.9Å for Fe^{3+}, Zn^{2+}, Cu^{2+}, Al^{3+} - mont and K-10- mont respectively. The metal content of each Fe^{3+}, Zn^{2+}, Cu^{2+}, Al^{3+} - mont catalysts were analyzed according to Vogel's procedure (Vogel, 1962) and was found to be 6.41, 1.82, 1.3 and 7.8% respectively.

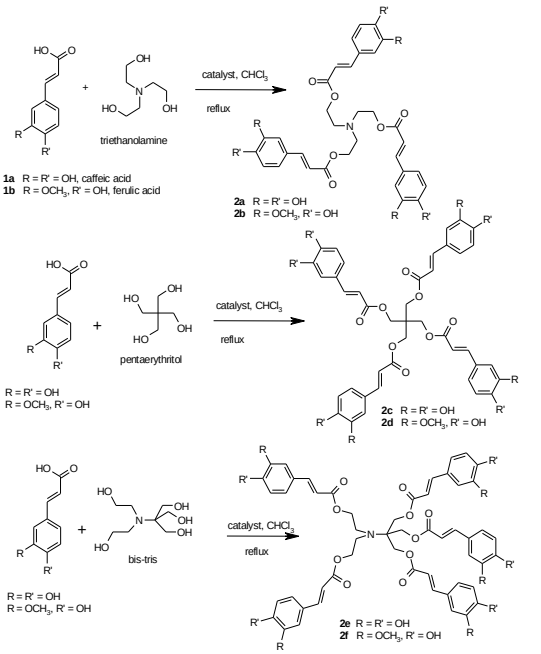
Esterification of phenolic acids

Two types of phenolic acids taken for esterification were hydroxy cinnamic acids (caffeic acid and ferulic acid) and hydroxy benzoic acids (gallic acid and protocatechuic acid). We had selected these four phenolic acids as all these acids are bioactive having antioxidant activities. Three hydroxyl compounds selected for the esterification were triethanol amine, pentaerythritol and bis-tris which are used as starting material for the construction of dendrimers. As we aimed to synthesize polyphenolic esters having a large number of phenolic moieties which might be responsible for antioxidant potentials, therefore we selected these three hydroxyl compounds from which lots of phenolic hydroxyl groups and ester linkages could be introduced in the synthesized polyphenolic esters. Scheme-1 and scheme-2 represent the typical synthesis of esters from hydroxy cinnamic acids and hydroxy benzoic acids respectively.

The esterification reactions were conducted by refluxing a mixture of phenolic acid, hydroxy compound and clay catalyst in chloroform followed by simple work-up procedure involving filtration of the solid catalyst and eventual evaporation of the solvent to obtain polyphenolic esters. This methodology was extended to a large scale (100mmol scale) by removing azeotrope water with a Dean-Stark apparatus. Although azeotropic removal of water is not warranted for small scale operations (1-5 mmol), it is essential to remove water from large scale reactions since the water formed inhibits the rate of reaction by blocking the acidic sites of montmorillonites.

A typical procedure for the preparation of polyphenolic ester, 2a

To a solution of caffeic acid (3mmol) and triethanolamine (1mmol) in 20ml chloroform, 150mg Fe^{3+}-mont was added. The mixture was then refluxed under Dean-Stark conditions for 8 hrs. After completion of the reaction (monitored by TLC) the reaction mixture was cooled and filtered. The filtrate was concentrated and purified by column chromatography over silica gel using hexane-ethyl acetate (3:1) as eluent to afford pure caffeic acid ester (76% yield).

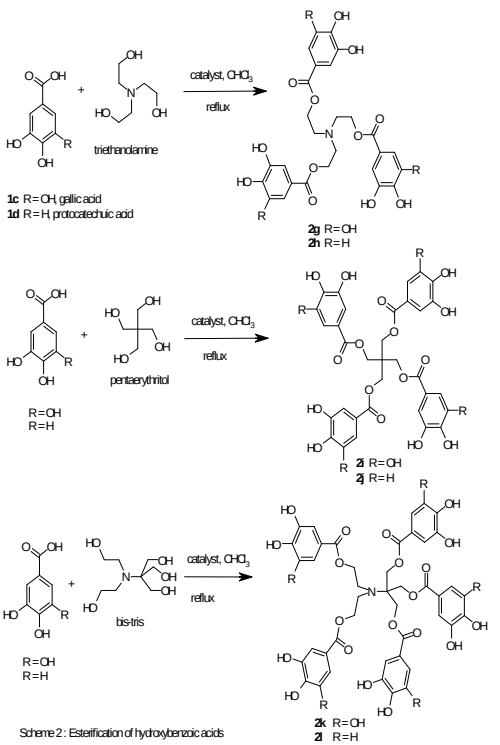


Scheme 1 : Esterification of hydroxycinnamic acids

Spectral and physical data of some selected compounds

O,O′,O″-tricaffeoyl-triethanolamine, (**2a)**: FTIR (KBr): 3300, 2920, 1703, 1622 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.8(6H, s, OH), 6.8-7.2 (9H, m, ArH), 6.42 (3H, d, J= 15.8 Hz, ArCH), 6.21 (3H, d, J=15.8 Hz, COCH), 4.42 (6H, t, J=3.7 Hz, $COOCH_2$), 3.08 (6H, t, J = 3.7 Hz, NCH_2). ^{13}C NMR (DMSO-d_6): δ 169.1, 155.2, 153.8, 144.3,

136.4, 132.2, 118.4, 116.9, 115.1, 68.1, 54.7. MS (m/z): 635 ($M^{\cdot+}$). Anal. Calcd. for $C_{33}H_{33}NO_{12}$: C, 62.36; H, 5.23; N, 2.20. Found: C, 62.31; H, 5.05; N, 2.19.



Scheme 2 : Esterification of hydroxybenzoic acids

O, O′,O″-triferuloyl-triethanolamine **(2b)**: FTIR (KBr): 3300, 2970, 1705, 1620 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.67(3H, s, OH), 6.8-7.4 (9H, m, ArH), 6.45 (3H, d, J= 15.8 Hz, ArCH), 6.22 (3H, d, J=15.8 Hz, COCH), 4.43 (6H, t, J=3.7 Hz, $COOCH_2$), 3.82 (9H, s, OCH_3), 3.10 (6H, t, J= 3.7 Hz, NCH_2). ^{13}C NMR (DMSO-d_6): δ 166.8, 148.5, 148.1, 139.1, 126.7, 121.7, 119.4, 115.8, 111.1, 65.8, 55.8, 54.1. MS(m/z): 677 ($M^{\cdot+}$). Anal, Calcd. for $C_{36}H_{39}NO_{12}$: C, 63.80; H, 5.80; N, 2.07. Found: C, 62.84; H, 5.71; N, 2.05.

O,O′,O″,O‴-tetracaffeoyl-pentaerythritol (**2c**): FTIR (KBr): 3350, 2915, 1710, 1620 cm^{-1}.^1H NMR (DMSO-d_6): δ 9.7(8H, s, OH), 6.7-7.2 (12H, m, ArH), 6.42 (4H, d, J= 15.8 Hz, ArCH), 6.20 (4H, d, J=15.8 Hz, COCH), 4.27 (8H, s, $COOCH_2$). ^{13}C NMR (DMSO-d_6): δ 168.6, 154.8, 152.7, 145.1, 133.4, 130.8, 117.3, 115.8, 114.7, 57.7, 26.4. MS(m/z): 784 ($M^{\cdot+}$). Anal. Calcd. for $C_{41}H_{36}O_{16}$: C, 62.75; H, 4.62. Found: C, 62.70; H, 4.61.

O,O′,O″,O‴-tetraferuloyl-pentaerythritol **(2d)**: FTIR (KBr): 3270, 2930, 1705, 1625 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.24(4H, s, OH), 6.7-7.3 (12H, m, ArH), 6.38 (4H, d, J= 15.8 Hz, ArCH), 6.13 (4H, d, J=15.8 Hz, COCH), 4.22 (8H, s, $COOCH_2$), 3.63 (12H, s, OCH_3). ^{13}C NMR (DMSO-d_6): δ 168.4, 158.2, 147.7, 138.8, 126.1, 121.3, 118.7, 116.6, 111.3, 65.5, 55.8, 26.2. MS(m/z): 840 ($M^{\cdot+}$). Anal, Calcd. for $C_{45}H_{44}O_{16}$: C, 64.28; H, 5.27. Found: C, 64.22; H, 5.21.

O,O′,O″,O‴,O⁗-pentacaffeoyl-bis-tris (**2e)**: FTIR (KBr): 3320, 2920, 1705, 1625 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.5(10H, s, OH), 6.9-7.4 (15H, m, ArH), 6.37 (5H, d, J= 15.8 Hz, ArCH), 6.15 (5H, d, J=15.8 Hz, COCH), 4.48 (4H, t, J= 3.7 Hz, $COOCH_2$), 3.91 (6H, s, $COOCH_2$), 2.64 (4H, t, J = 3.7 Hz, NCH_2). ^{13}C NMR (DMSO-d_6): δ 170.2, 153.8, 151.2, 140.7, 136.4, 131.3, 128.4, 116.3, 112.1, 72.7, 70.3, 49.2, 43.6. MS(m/z): 1019 ($M^{\cdot+}$). Anal. Calcd. for $C_{53}H_{49}NO_{20}$: C, 62.41; H, 4.84; N, 1.37. Found: C, 62.39; H, 4.78; N, 1.36.

O,O′,O″,O‴,O⁗-pentaferuloyl-bis-tris (**2f)**: FTIR (KBr): 3300, 2915, 1710, 1620 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.6(5H, s, OH), 6.8-7.3 (15H, m, ArH), 6.34 (5H, d, J= 15.8 Hz, ArCH), 6.12 (5H, d, J=15.8 Hz, COCH), 4.52 (4H, t, J= 3.7 Hz, $COOCH_2$), 3.95 (6H, s, $COOCH_2$), 3.68 (15H, s, OCH_3), 2.68 (4H, t, J= 3.7 Hz, NCH_2). ^{13}C NMR (DMSO-d_6): δ 169.4, 149.6, 148.2, 138.7, 126.3, 121.3, 118.7, 116.8, 110.8, 72.6, 70.3, 55.8, 49.2, 44.2. MS(m/z): 1089 ($M^{\cdot+}$). Anal, Calcd. for $C_{58}H_{59}NO_{20}$: C, 63.91; H, 5.46; N, 1.28. Found: C, 63.88; H, 5.40; N, 1.28.

O,O′,O″-trigalloyl-triethanolamine (**2g)**: FTIR (KBr): 3295, 2920, 1720 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.5(9H, s, OH), 7.12 (6H, s, ArH), 4.43 (6H, t, J= 3.7 Hz, $COOCH_2$), 3.11 (6H, t, J = 3.7 Hz, NCH_2). ^{13}C NMR (DMSO-d_6): δ 168.2, 146.4, 137.3, 122.1, 111.5, 65.3, 54.3. MS (m/z): 605 ($M^{\cdot+}$). Anal. Calcd. for $C_{27}H_{27}NO_{15}$: C, 53.56; H, 4.49; N, 2.31. Found: C, 53.52; H, 4.47; N, 2.30.

O,O′,O″-triprotocatechuoyl-triethanolamine **(2h)**: FTIR (KBr): 3295, 2930, 1715 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.35(6H, s, OH), 6.9-7.2 (9H, m, ArH), 4.38 (6H, t, J= 3.7 Hz, $COOCH_2$), 3.09 (6H, t, J = 3.7 Hz, NCH_2). ^{13}C NMR (DMSO-d_6): δ 144.8, 139.5, 126.7, 121.8, 116.4, 114.3, 65.6, 54.5. MS(m/z): 557 ($M\cdot^+$). Anal, Calcd. for $C_{27}H_{27}NO_{12}$: C, 58.17; H, 4.88; N, 2.51. Found: C, 58.19; H, 4.81; N, 2.47.

O,O′,O″,O‴-tetragalloyl-pentaerythritol (**2i)**: FTIR (KBr): 3300, 2925, 1725 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.1(12H, s, OH), 7.21 (8H, s, ArH), 4.22 (8H, s, $COOCH_2$). ^{13}C NMR (DMSO-d_6): δ 170.1, 149.3, 138.7, 120.6, 110.8, 62.5, 26.7. MS (m/z): 744 ($M\cdot^+$). Anal. Calcd. for $C_{33}H_{28}O_{20}$: C, 53.23; H, 3.79. Found: C, 53.20; H, 3.73.

O,O′,O″,O‴-tetraprotocatechuoyl-pentaerythritol **(2j)**: FTIR (KBr): 3300, 2920, 1710 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.28 (8H, s, OH), 6.9-7.3 (12H,m, ArH), 4.18 (8H, s, $COOCH_2$). ^{13}C NMR (DMSO-d_6): δ 168.6, 145.1, 140.8, 126.2, 122.3, 117.2, 114.4, 64.7, 26.8. MS(m/z): 680 ($M\cdot^+$). Anal, Calcd. for $C_{33}H_{28}O_{16}$: C, 58.24; H, 4.15. Found:C , 58.28; H, 4.08.

O,O′,O″,O‴,O⁗-pentagalloyl-bis-tris (**2k)**: FTIR (KBr): 3290, 2920, 1715 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.3(15H, s, OH), 7.05 (10H, s, ArH), 5.10 (4H, t, J= 3.7 Hz, $COOCH_2$), 4.65(6H,s, $COOCH_2$), 3.23 (4H, t, J = 3.7 Hz, NCH_2). ^{13}C NMR (DMSO-d_6): δ 168.6, 145.2, 139.1, 123.4, 112.2, 71.3, 53.3, 46.8. MS(m/z): 969 ($M\cdot^+$). Anal. Calcd. for $C_{43}H_{39}NO_{25}$: C, 53.26; H, 4.05; N, 1.44. Found: C, 53.20; H, 4.01; N, 1.42.

O,O′,O″,O‴,O⁗-pentaprotocatechuoyl-bis-tris **(2l)**: FTIR (KBr): 3300, 2920, 1710 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.45(10H, s, OH), 6.9-7.2 (15H, m, ArH), 5.22 (4H, t, J= 3.7 Hz, $COOCH_2$), 4.73 (6H,s, $COOCH_2$), 3.35 (4H, t, J = 3.7 Hz, NCH_2). ^{13}C NMR (DMSO-d_6): δ 168.6, 145.3, 139.7, 126.6, 122.5, 117.8, 114.7, 71.6, 49.4, 44.3. MS(m/z): 889 ($M\cdot^+$). Anal, Calcd. for $C_{43}H_{39}NO_{20}$: C, 58.05; H, 4.42; N, 1.57. Found: C, 58.11; H, 4.35; N, 1.55.

RESULTS AND DISCUSSION

Esterification reactions of caffeic acid with hydroxyl compounds under reflux were carried out using various montmorillonites and the results of esterification were summarized in Table1. Among these various clay catalysts Fe^{3+}- mont exhibited the highest catalytic activity for esterification (entry 5, 11 and 17, Table 1). In contrast, when K-10- montmorillonite was used alone the yields of the products were very lower.

Table 1 : Esterification of caffeic acid using various montmorillonites

Hydroxy compound & the molar ratio[1)]	Entry	Catalyst	Reaction time (hr)	Yield[2)] (%)
Triethanolamine (3 : 1)	1	K-10-Mont	8	8
	2	Al^{3+}-Mont	8	11
	3	Cu^{2+}-Mont	8	37
	4	Zn^{2+}-Mont	8	38
	5	Fe^{3+}-Mont	8	76
	6	No catalyst	8	0
Pentaerythritol (4 : 1)	7	K-10-Mont	10	5
	8	Al^{3+}-Mont	10	6
	9	Cu^{2+}-Mont	10	31
	10	Zn^{2+}-Mont	10	36
	11	Fe^{3+}-Mont	10	71
	12	No catalyst	10	0
Bis-tris (5 : 1)	13	K-10-Mont	11	2
	14	Al^{3+}-Mont	11	3
	15	Cu^{2+}-Mont	11	20
	16	Zn^{2+}-Mont	11	31
	17	Fe^{3+}-Mont	11	69
	18	No catalyst	11	0

[1)] phenolic acid : hydroxyl compound

[2)] yields are calculated on the basis of isolated product

The metal exchanged montmorillonites were easily prepared from the readily available and inexpensive metal chlorides(viz. $FeCl_3$, $ZnCl_2$, $CuCl_2$ and $AlCl_3$) and K-10- mont clay by the reported method.[25] The decreasing order of activity of the catalysts towards esterification was found to be Fe^{3+}>Zn^{2+}>Cu^{2+}>Al^{3+}-mont> K-10- montmorillonite. Metal exchanged montmorillonites showed higher catalytic activities than natural montmorillonite due to highly mesophorous structure compatible for large reacting molecules and high density of acidic sites within interlayer space. Further, Fe^{3+}- mont exhibited higher catalytic activity than other metal exchanged mont as intercalated Fe^{3+} complex generates higher number of protons than other metal ions. The catalytic activities of these catalysts were studied for three cycles and no loss of activity of any catalyst was found. The yields were almost same from the fresh catalyst to the third recycled catalyst.

Table 2 shows the esterification of the four phenolic acids when treated with the three hydroxyl compounds under reflux in presence of Fe^{3+}- mont catalyst. Esterification over Fe^{3+}- mont catalyst results excellent yields. The prominent catalysis of Fe^{3+}- mont can be ascribed to its strong acidity and an expansion of the interlayer space under reaction conditions. The spent Fe^{3+}- mont catalyst was readily separated from the reaction mixture by a simple filtration. The isolated Fe^{3+}- mont could be reused without an appreciable loss of its high catalytic activity. It was observed that hydroxy benzoic acids required comparatively more reaction time than hydroxy cinnamic acids to transform into corresponding esters. Further X-ray diffraction studies of various metal exchanged mont showed the retention of the layered structure of K-10- montmorillonite.

In conclusion, we have developed a simple methodology using metal exchanged montmorillonite clay as strong solid acid catalyst for the esterification of bio active phenolic acids which provide a green protocol to replace homogeneous acids. The catalyst serves as efficient, rapid and inexpensive heterogeneous catalyst to synthesize polyphenolic esters. Besides these, the ease of operation, the simple work up procedure and environmental advantage make the process very useful. Further studies on the application of metal exchanged montmorillonites to synthesize new dendritic polyphenolic esters and amides having significant antioxidant potentials are in progress.

Table 2: Esterification of phenolic acid using Fe^{3+}- Mont

Hydroxy compound & the molar ratio[1)]	Entry	Phenolic acid	Product	Reaction time (hr)	Yield[2)] (%)
Triethanolamine (3 : 1)	1	1a	2a	8	76
	2	1b	2b	8	73
	3	1c	2g	10	61
	4	1d	2h	10	63
Pentaerythritol (4 : 1)	5	1a	2c	10	71
	6	1b	2d	10	75
	7	1c	2i	13	52
	8	1d	2j	13	57
Bis-tris (5 : 1)	9	1a	2e	11	69
	10	1b	2f	11	71
	11	1c	2k	14	55
	12	1d	2l	14	58

[1)] phenolic acid : hydroxy compound
[2)] yields are calculated on the basis of isolated product

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