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The Synthesis of Gallic Esters of Higher Fatty Alcohols under Solvent-Free Conditions Using Microwave Irradiation

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Abstract: The reactions of gallic acid with higher fatty alcohols are acceterated by microwaves under solvent-free conditions in the presence of *p*-toluenesulfonic acid to afford a high yield synthesis of higher fatty alcohol gallates. Montmorillonite K 10 are less efficient.

Keywords: Gallic ester, Montmorillonite K 10, microwave irradiation.

Higher fatty alcohol gallic esters are reported as fine food antioxidants[1] and color developing agents[2] for heat sensitive recording paper or carbonless paper. They are usually synthesized by one of two main methods: esterification of gallic acid[3] and transesterification of methyl or ethyl esters[4]. The main disadvantages of some of those methods are the use of uncommon reagents and difficult work-up. We wish to report a simple synthetic procedure utilizing microwave irradiation[5,6] under solvent-free conditions, different acids, including Montmorillonite K 10 and *p*-toluenesulfonic acid (PTSA), were tested (**Scheme 1**). The results are summarized in **Table 1**.

Scheme 1

$$(HO)_3C_6H_2COOH + HOC_nH_{2n+1} \xrightarrow{\text{catalyst}} (HO)_3C_6H_2COOC_nH_{2n+1} + H_2O$$

n = 8, 12, 14, 16, 18

Table 1. Esterification of gallic acid with higher fatty alcohols using microwaves

Alcohols	Esters	Time (min)	K-10 Yield (%)	PTSA Yield (%)	m.p. (℃)
$C_8H_{17}OH$	$(HO)_3C_6H_2COOC_8H_{17}$	5	47	89	93-94
$C_{12}H_{25}OH$	$(HO)_3C_6H_2COOC_{12}H_{25}$	7	49	93	95-97
$C_{14}H_{29}OH$	$(HO)_3C_6H_2COOC_{14}H_{29}$	7	38	90	98-99
$C_{16}H_{33}OH$	$(HO)_3C_6H_2COOC_{16}H_{33}$	9	35	88	98-100
$C_{18}H_{37}OH$	$(HO)_3C_6H_2COOC_{18}H_{37}$	9	29	86	101-103

When compared to other experimental conditions, our approach reduces considerably the longer reaction times and large quantities of aromatic solvents required in the conventional solution phase chemistry that entails the azeotropic removal of water using Dean-Stark apparatus and provides better product yields. The most favourable reaction conditions involved the use of PTSA, which led to good yields. K-10 Montmorilonite was found to be less efficient.

Our protocol developed for higher fatty alcohol gallic esters is extendible to the esterification of higher fatty alcohols with some organic acids which are insoluble in the organic solvents used by ordinary esterification, for example, fumaric acid, malic acid, tartaric acid and citric acid, *etc.*. The results are given in **Table 2**.

Table 2 PTSA catalyzed synthesis of organic acid dodecanol esters using microwaves

Organic acid	Fumaric acid	Tartaric acid	Malic acid
Ester	Dodecyl fumarate	Dodecyl tartrate	Dodecyl malate
Time (min)	8	5	6
Yield (%)	97	83	86
mp (℃)	46-47	63-65	36-37

General procedure for esterifications with PTSA

Gallic acid (0.01mol), octadecanol (0.01mol) and PTSA (2.0g) were impregnated on aluminum oxide (1.0g) (*via* solution in acetone or dichloromethane and evaporation of solvent). The mixture was irradiated in a microwave oven at middle power for 9 min. Upon completion of the reaction, as followed by TLC examination, the product is extracted into acetone or dichloromethane (3×10ml), the solvent was removed under reduced pressure. The product was successively washed with 10% $NaHCO_3$ and H_2O, and recrystallized from acetone to give octadecanol gallate in 86% yield. IR (KBr, ν, cm^{-1}): 3300-3550 (OH),1720 (C=O), 1200 (C-O), 1100 (O-CH_2), ^{1}HNMR (δ_H, ppm): 7.2~7.6 (s, 2H, C_6H_2), 7.9 (s, 3H,OH), 4.2 (t, 2H, OCH_2), 1.3~1.8 (m, 32H, CH_2), 1.1 (t , 3H, CH_3). Elemental analysis (%), $C_{25}H_{42}O_5$, Calcd.: C, 71.05; H, 10.02. Found: C, 70.86; H, 9.94.

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