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RESEARCH ARTICLE

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Synthesis of methyl 12-benzoyldehydroabietate in ionic liquid

Abstract In the presence of the ionic liquid [bmim]Br/$AlCl_3$ as green reaction medium, methyl 12-benzoyldehydroabietate was synthesized through Friedel-Crafts acylation reactions on the aromatic ring of methyl dehydroabietate. The optimum synthetic conditions of the target product were found to be as follows: molar ratio of methyl dehydroabietate to [bmim]Br to $AlCl_3$ to benzoyl chloride 1:4:8:8, reaction temperature 40°C, reaction time 2 h. The target product was analyzed and characterized by means of IR, MS, NMR and elemental analysis. The results show that this novel method has the advantages of mild condition, short reaction time and environmental benignity.

Keywords ionic liquid, dehydroabietic acid, Friedel-Crafts acylation, methyl 12-benzoyldehydroabietate

0 Introduction

Rosin is an abundant natural renewable resource in China, unfortunately, most of which is mainly exported in the form of raw material, and has a very low deep processing [1]. Dehydroabietic acid is the dominant component of disproportionated rosin produced by catalytic disproportionation of rosin. Wide applications of dehydroabietic acid can be expected in the field of synthetic chemicals due to its unique characteristics such as stable properties, strong antioxidant ability and large specific rotatory power [2–5]. In recent years, in order to prepare rosin-based functional compounds with high additional value, people have paid more attention to the modification of dehydroabietic acid. Many important rosin-based arone intermediates have been prepared through the Friedel-Crafts reaction on the aromatic ring of dehydroabietic acid [6,7]. Recently, Li *et al.* [8] reported on the structure of methyl 12-benzoyldehydroabietate, which was synthesized under the conditions of methyl dehydroabietate and benzoyl chloride as raw materials, 1, 1, 2, 2-tetrachloroethane and $AlCl_3$ as solvent and catalyst, respectively, room temperature, and reaction time 24 h. The yield amounted to 81%.

In recent years, there have been increasing reports related to room-temperature ionic liquids as reaction media in green chemistry. Compared with the traditional organic solvents, ionic liquids have lots of advantages such as non-volatibility, low toxicity, good heat stability, non-flammation, unique solubility, facility-designed structure and so on [9,10]. More and more researches have indicated that chloroaluminate ionic liquids can be used as solvents and catalysts in Friedel-Crafts acylation, and own distinct advantages such as benignity to environment, mild condition, good selectivity and high yield [11–13].

In this paper, we attempted to synthesize methyl 12-benzolydehydroabietate via the Friedel-Crafts acylation reaction of methyl dehydroabietate with benzoyl chloride in ionic liquid 1-butyl-3-methylimidazolium bromide ([bmim]Br)/$AlCl_3$. The aim of this study was to widen the application fields of ionic liquids and also to provide another new approach for the greening and the diversification of deep processing of rosin.

1 Experimental

1.1 Synthetic route of methyl 12-benzoyldehydroabietate

Methyl dehydroabietate was prepared via acyl chloration and subsequent methanolysis of dehydroabietic acid at first. Then, methyl 12-benzoyldehydroabietate was synthesized by the Friedel-Crafts acylation reaction of methyl dehydroabietate with benzoyl chloride in ionic liquid [bmim]Br/$AlCl_3$ (Scheme 1).

1.2 Materials and equipments

Dehydroabietic acid (made in our laboratory [14], the content of dehydroabietic acid was 95% by GC); benzene

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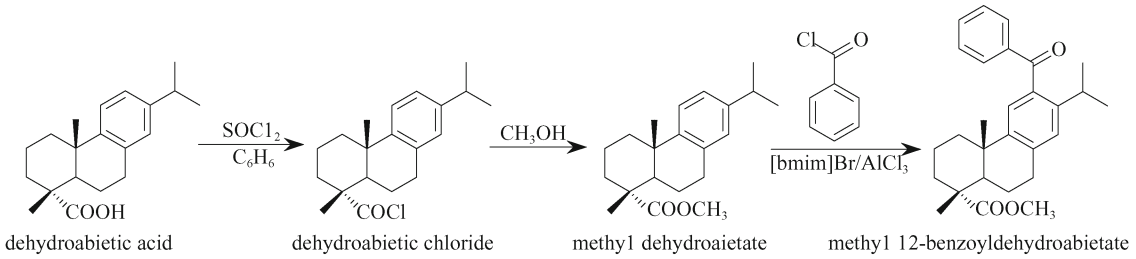


Scheme 1 Synthetic route of methyl 12-benzoyldehydroabietate

(AR), $SOCl_2$ (AR), methanol (AR), benzoyl chloride (AR), anhydrous $AlCl_3$ (AR), *N*-methylimidazole (Industrial Grade, the purity > 98%), n-bromide butane (CP), and hydrochloric acid (AR) were all purchased from the local market.

Ordinary pressure microwave-assisted synthesis/extraction apparatus (MAS-I), produced by Shanghai Sineo Microwave Chemistry Technology Co., Ltd., China, was employed in the synthesis of ionic liquid intermediate 1-butyl-3-methylimidazolium bromide ([bmim]Br). FT-IR spectra were recorded on a Nicolet Nexus 470 spectrometer (Nicolet Co., Ltd., USA). GC-MS analysis was performed using a GCMS-QP5050A instrument (Shimadzu Ltd., Japan), GC test was carried out using a HP6890 chromatograph (Agilent Co., Ltd., USA). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on an AVANCE AV 500 instrument (Bruker Co., Ltd., Switzerland, $CDCl_3$ as solvent). Elemental analysis was obtained using a PE2400 II element analyzer (Perkin Elmer Co., Ltd., USA).

1.3 Synthesis of ionic liquid [bmim]Br/$AlCl_3$

1.3.1 Synthesis of 1-butyl-3-methylimidazolium ([bmim]Br) [15]

n-Butanebromide (22.4 mL, 0.21 mol) and N-methylimidazole (15 mL, 0.19 mol) were added to a 100 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. The mixture was irradiated for 30 min at 60°C in a microwave reactor until a clear single phase was obtained. The acetonitrile was added to the resulting ionic liquid and this phase was washed thrice with ethyl acetate to remove un-reacted starting materials. The lower (acetonitrile) phase was collected and put in a 100 mL round-bottomed flask to remove acetonitrile and residual ethyl acetate by rotary evaporation at 70°C for 2 h. The product, [bmim]Br, was obtained as a slightly colorless, viscous oil in 94.3% yield and may be crystalline at about 20°C. The product was characterized by FT-IR and ^{1}H-NMR.

1.3.2 Synthesis of [bmim]Br/$AlCl_3$ [16,17]

Anhydrous $AlCl_3$ was added slowly, while stirring, to a three-necked flask containing [bmim]Br at ambient temperature. After 2 h, a transparent, light yellow ionic liquid [bmim]B/$AlCl_3$ was obtained and was kept in a vacuum desiccator.

1.3.3 Synthesis of dehydroabietic chloride [18]

In a 250 mL three-necked round-bottom flask fitted with a spherical condenser connecting to a gas inlet adsorber using 10% NaOH as absorption liquid, dropping funnel and thermometer, $SOCl_2$ (11.6 mL, 0.16 mol) was dropped slowly, with stirring for 30 min, to a solution of dehydroacietic acid (20.0 g, 0.07 mol) in benzene (30 mL) at room temperature. Then, the mixture was heated at 75°C–85°C for 3 h. After cooling to room temperature, the solvent and excess of $SOCl_2$ were removed by distillation at atmospheric pressure, followed by distillation under reduced pressure. The product was obtained in 98.1% yield, which was stored under dry conditions. The product was characterized by FT-IR.

1.3.4 Synthesis of methyl dehydroabietate [18]

Methanol (45 mL, 1.11 mol) was added dropwise to dehydroabietic chloride (19.8 g, 0.06 mol) in the above apparatus with rapid stirring at 70°C to 75°C for at least 3 h until no HCl gas was generated. The excess methanol was removed under reduced pressure. After cooling to room temperature, the product was obtained as a slightly brown yellow, viscous semi-solid in 98.1% yield. The product was characterized by FT-IR, and its purity was 95.3% by GC.

1.3.5 Synthesis of methyl 12-benzoyldehydroabietate

A certain amount of ionic liquid [bmim]Br/$AlCl_3$ was placed in a 250 mL three-necked flask equipped with a spherical condenser connected to a gas absorption device, a dropping funnel and an electric agitator. With stirring, 2.5 g methyl dehydroabietate was added to the reaction system kept in an ice-salt bath (about −5°C), and then a quantitative redistilled benzoyl chloride was dropped slowly. Then, the system was heated in a water bath to the presetting reaction temperatures for some time. After reaction and with stirring, a solution of 4 mol/L hydrochloric acid was added, and a yellow viscous substance was separated. The substance was washed with deionized

water until the washing water was neutral and the crude product was obtained. The qualitative analysis of the crude product was carried out by GC-MS technique combined with the orientation law of polysubstituted benzene, and its quantitative analysis was accomplished by GC, so the yield of the target product was calculated.

The crude product was dissolved in appropriate diethyl ether and dried over anhydrous $MgSO_4$ for several hours, followed by removing the diethyl ether with a rotary evaporator. Recrystallization from methanol afforded white needle crystals of methyl 12-benzoyldehydroabietate with mp 152°C–153°C (lit.[8],152.6°C–153.5°C). The target product was analyzed and characterized by means of IR, MS, NMR and elemental analysis.

2 Results and discussion

2.1 Investigation of synthetic conditions of methyl 12-benzoyldehydroabietate

According to the orientation law of polysubstituted benzene, the electrophilic substitution of the benzoyl group on the aromatic ring of methyl dehydroabietate will mainly take place at 12-position and scarcely at 11-position or 14-position. The analytic result of the target product was in good agreement with that predicted from theory, indicating that the ionic liquid [bmim]Br/$AlCl_3$ could be used as solvent and catalyst of the Friedel-Crafts acylation reaction, and the reaction in the ionic liquid was in accord with general chemical laws as well.

Owing to the structural characteristics of dehydroabietic acid, some side reactions such as deisopropylation [13,19] easily occurred in the presence of anhydrous $AlCl_3$ as catalyst. Therefore, the reaction conditions could have direct effects on the yield of the target product.

2.1.1 Effect of molar fraction of $AlCl_3$ in [bmim]Br

Acylation reaction of methyl dehydroabietate with benzoyl chloride was investigated in the ionic liquid [bmim]Br/$AlCl_3$ and the molar fraction of $AlCl_3$ $0.67 \geqslant x \geqslant 0.50$. The results are listed in Table 1.

Table 1 Effect of molar fraction of $AlCl_3$ in [bmim]Br on the yield of the target product

n	yield of the target product/%
0.50	0
0.60	24.0
0.67	50.5
0.71	48.8

Reaction conditions: molar ratio of methyl dehydroabietate to [bmim]Br to benzoy chloride = 1:4:8; reaction temperature: 40°C; reaction time: 1 h

As can be seen from Table 1, the reaction yield was dependent on the molar fraction of $AlCl_3$. The yield of the target product increased remarkably with the increase in molar fraction of $AlCl_3$, and the acidity of the ionic liquid [bmim]Br/$AlCl_3$ could be varied through a wide range depending on the proportion of $AlCl_3$ to organic base. If $n < 0.5$, the ionic liquid is Lewis basic. If $n = 0.5$, the ionic liquid is Lewis neutral. If $n > 0.5$, the ionic liquid is Lewis acidic [20]. The results show that no reaction took place when n was equal to 0.5. By increasing the n value, the acidity was raised. When n value reached 0.67 [21], the acylation reaction of methyl dehydroabietate was effectively catalyzed because the Friedel-Crafts acylation reaction was carried out via carbocation mechanism in the presence of a strong acid as catalyst; whereas, when n was 0.71, the yield of the target product was slightly decreased. Therefore, 0.67 was the best for the reaction.

2.1.2 Effect of reaction time

The effect of reaction time on the yield of acylation reaction in [bmim]Br/$AlCl_3$ ($n = 0.67$) is shown in Table 2. As can be seen, the reaction time had a remarkable effect on the yield of the target product. A short time was not helpful for the accomplishment of the reaction, whereas too long a time would lead to more side products. So the optimum reaction time was found to be 2 h.

Table 2 Effect of reaction time on the yield of the target product

reaction time/h	yield of the target product/%
1	50.5
2	64.0
3	39.6
4	18.0

Reaction conditions: molar ratio of methyl dehydroabietate to [bmim]Br to $AlCl_3$ to benzoyl chloride = 1:4:8:8; reaction temperature 40°C

2.1.3 Effect of molar ratio of methyl dehydroabietate to benzoyl chloride

The effect of molar ratio of methyl dehydroabietate to benzoyl chloride on the yield of the target product was also investigated. The results are shown in Table 3. They demonstrate that with an increase in molar ratio, the yield of the target product increased rapidly at first and then decreased. The maximum yield of the target product was obtained at the molar ratio of methyl dehydroabietate to benzoyl chloride 1:8. It was concluded that Friedel-Crafts acylation could not be promoted effectively by a low amount of benzoyl chloride, whereas an excessive amount of benzoyl chloride would lead to more side reactions. Hence, the optimal molar ratio of methyl dehydroabietate to benzoyl chloride was selected to be 1:8.

Table 3 Effect of molar ratio of methyl dehydroabietate to benzoyl chloride on the yield of the target product

n(methyl dehydroabietate) : *n*(benzoyl chloride)	yield of the target product/%
1:2	7.7
1:4	20.8
1:6	42.3
1:8	64.0
1:10	62.3

Molar ratio of methyl dehydroabietate-to-[bmim]Br-to-$AlCl_3$ 1:4:8, reaction temperature 40°C, reaction time 2 h

2.1.4 Effect of reaction temperature

The effect of reaction temperature on the yield of acylation reaction in [bmim]Br/$AlCl_3$ (n = 0.67) is shown in Table 4. As can be seen, the yield of the target product increased obviously with the increase in reaction temperature at first and then decreased slowly, implying that both low and high temperatures were not helpful for the reaction. Therefore, 40°C was the optimal reaction temperature.

Table 4 Effect of reaction temperature on the yield of the target product

reaction temperature/°C	yield of the target product/%
30	21.2
40	64.0
50	56.1
60	30.9

Molar ratio of methyl dehydroabietate-to-[bmim]Br-to-$AlCl_3$-to-benzoyl chloride 1:4:8:8, reaction time 2 h

2.1.5 Effect of reuse of the ionic liquid

The reusability of the ionic liquid was also studied. Because [bmim]Br is water soluble, after reaction, the crude product could be washed with water. After filtration, [bmim]Br was easily recovered by removing water under vacuum evaporation at 75°C for 2 h. Before reuse, some amount of $AlCl_3$ was added to the recovered ionic liquid.

As can be seen from Table 5, the yield of the target product decreased slightly as the ionic liquid was reused four times, indicating that the ionic liquid can be recycled for the Friedel-Crafts acylation reaction.

Table 5 Effect of reuse of ionic liquid on the yield of the target product

reuse times of ionic liquid	yield of the target product/%
1	64.0
2	62.7
3	62.5
4	60.8

Molar ratio of methyl dehydroabietate-to-[bmim]Br-to-$AlCl_3$-to-benzoyl chloride 1:4:8:8, reaction temperature 40°C, reaction time 2 h

2.2 Characterization of [bmin]Br

2.2.1 FT-IR analysis of [bmim]Br

The FT-IR spectrum of [bmim]Br is shown in Fig. 1. The peaks at 3160 and 3120 cm^{-1} correspond to the C–H stretching vibrations in the imidazole ring, and 2966, 2942, 2878 cm^{-1} are attributed to the stretching vibrations of C–H in the side alkyl chain. The peaks at 1570 and 1466 cm^{-1} are related to the vibrations of the whole imidazole ring. The peaks at 1384 cm^{-1} and 1170 cm^{-1} are assigned to the C–H bending vibration in the methyl group, and the C–H in-plane bending vibration in the aromatic ring, respectively. The peak at 753 cm^{-1} is characteristic of the C–H stretching vibration in the CH_2 of the long chain. Obviously, the IR spectral data support the structure of [bmim]Br [22,23].

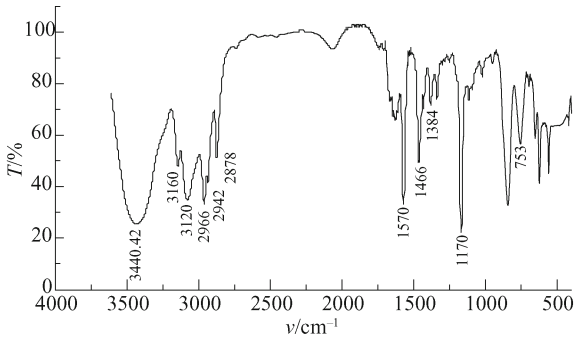
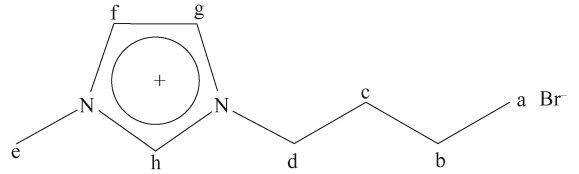


Fig. 1 IR spectrum of [bmim]Br

2.2.2 ^{1}H-NMR analysis of [bmim]Br



[bmim] Br^-

^{1}H-NMR spectral data of [bmim]Br are listed as follows: (500 MHz, $CDCl_3$) δ: 0.89 (t, 3H, H-a), 1.23 (m, 2H, H-b), 1.79 (m, 2H, H-c), 4.15 (t, 2H, H-d), 3.90 (s, 3H, H-e), 7.66 (s, 1H, H-f), 7.57(s, 1H, H-g), 9.18(s, 1H, H-h). These data are in good agreement with the values in literature [15] and further confirm the structure of [bmim]Br.

2.3 Characterization of methyl 12-benzoyldehydroabietate

2.3.1 FT-IR analysis of methyl 12-benzoyldehydroabietate

The FT-IR spectrum of methyl 12-benzoyldehydroabietate is shown in Fig. 2. The peaks at 3056 and 3008 cm^{-1} are

attributed to the C–H stretching vibrations in the aromatic ring, and 2947, 2926 and 2870 cm^{-1} correspond to C–H stretching vibrations in the CH_3 and CH_2 groups. The strong and complete peak at 1720 cm^{-1} is assigned to the characteristic C=O stretching vibration in the ester group, and the peaks at 1251, 1225 and 1180 cm^{-1} are assigned to C–O stretching vibrations in the ester group. The peaks at 1599, 1463 and 1448 cm^{-1} belong to the vibrations in the skeletal aromatic ring. The strong and complete peak at 1669 cm^{-1} is the characteristic absorption of C=O in arone. The IR spectrum confirmed successful synthesis of methyl 12-benzoyldehydroabietate in ionic liquid.

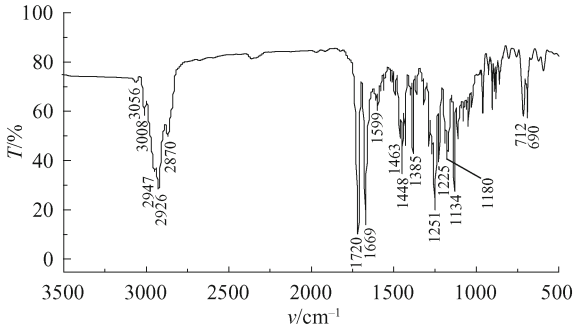
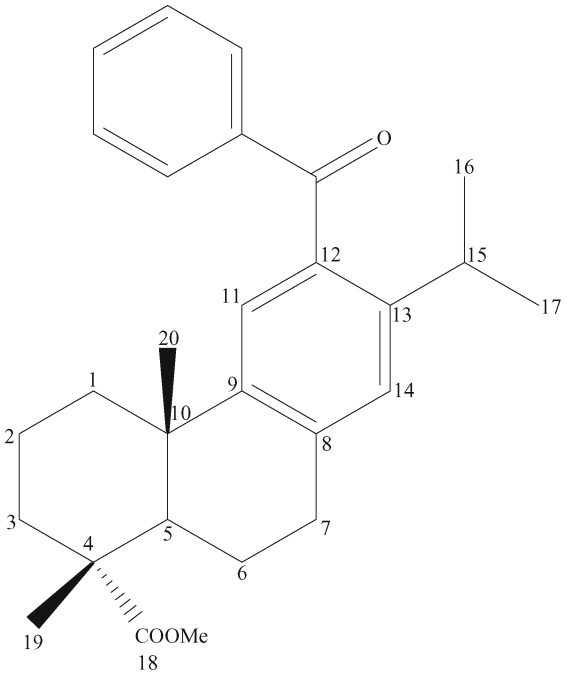


Fig. 2 IR spectrum of methyl 12-benzoyldehydroabietate

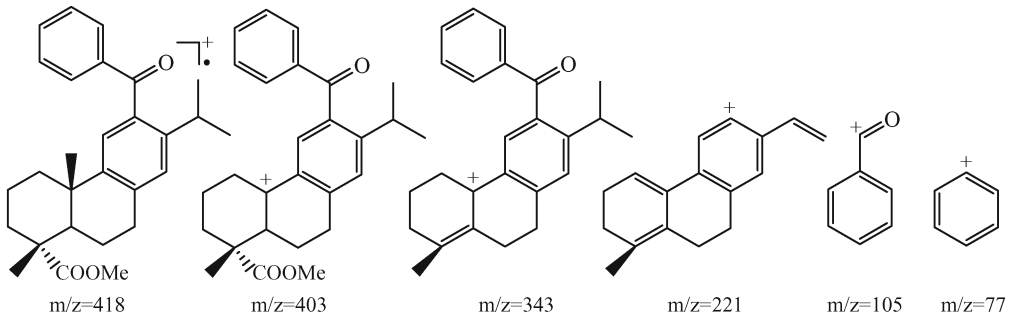
2.3.2 GC-MS analysis of methyl 12-benzoyldehydroabietate

As can be seen from the TIC, the purity of methyl 12-benzoyldehydroabietate amounted to 99.82%. Following molecular fragment ion peaks, the molecular structure ($m/z = 105$ is the base peak) could be deduced from its MS spectrum:

2.3.3 ^{1}H-NMR and ^{13}C-NMR analysis of methyl 12-benzoyldehydroabietate



The ^{1}H-NMR and ^{13}C-NMR data of methyl 12-benzoyldehydroabietate are listed as follows: ^{1}H-NMR



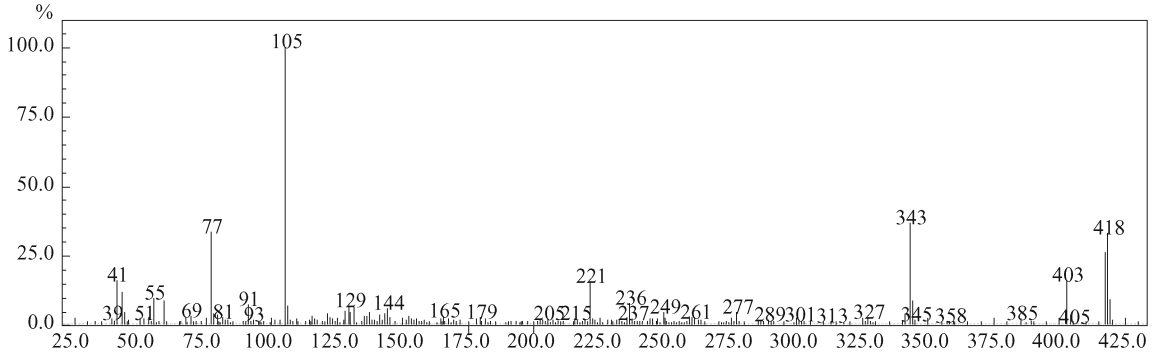


Fig. 3 MS spectrum of methyl 12-benzoyldehydroabietate

(500 MHz, $CDCl_3$, δ):1.17 (s, 3H, 10-CH_3), 1.21 (d, 6H, 16-CH_3, 17-CH_3), 1.29(s, 3H, 4-CH_3), 1.47-1.50 (m, 2H, 1-H, 6-H), 1.62-1.67 (m, 4H, 2-H_2, 3-H_2), 1.75-1.77 (m, 1H, 6-H), 2.16 (d, 1H, 1-H), 2.26 (d, 1H, 5-Hα), 2.97 (m, 2H, 7-H_2), 3.06 (m, 1H, 15-H), 3.70 (s, 3H, $COOCH_3$), 7.10 (s, 1H, 14-H), 7.28 (m, 1H), 7.47 (m, 2H), 7.59 (s, 1H, 11-H), 7.83 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 16.5 (4-CH_3), 18.4 (C-2), 21.6 (C-6), 24.0 and 24.2 (C-16, 17), 25.0 (10-CH_3), 29.5 (C-15), 30.0 (C-7), 36.6 (C-3), 37.0 (C-10), 37.8 (C-l), 44.9 (C-5), 47.6 (C-4), 51.9 (OCH_3), 124.2 (C-11), 126.5 (C-14), 128.3 (C-Ar), 130.2 (C-Ar), 133.0 (C-Ar), 135.8 (C-Ar), 137.5 (C-12), 138.4 (C-8), 144.4 (C-13), 146.3 (C-9), 179.0 (C-18), 199.1 (12-CO). These data further confirmed the structure of methyl 12-benzoyldehydroabietate

2.3.4 Elemental analysis of methyl 12-benzoyldehydroabietate

The molecular formula of methyl 12-benzoyldehydroabietate is $C_{28}H_{34}O_3$. The result of elemental analysis is as follows: calculated for C 80.35, H 8.19, and found for C 80.34, H8.16. These data are very consistent with each other.

3 Conclusions

In the presence of ionic liquid [bmim]Br/$AlCl_3$ as green reaction medium, methyl 12-benzoyldehydroabietate was synthesized through Friedel-Crafts acylation reactions of methyl dehydroabietate with benzoyl chloride. The optimum synthetic conditions were found to be as follows: molar ratio of methyl dehydroabietate-to-[bmim]Br-to-$AlCl_3$-to-benzoyl chloride 1:4:8:8, reaction temperature 40°C, reaction time 2 h. Compared with the method described in literature, this novel method has the advantages of mild condition, short reaction time and environmental benignity. The ionic liquid could be reused more than three times.

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