One-step Synthesis of Dibutyl Furandicarboxylates from Galactaric Acid

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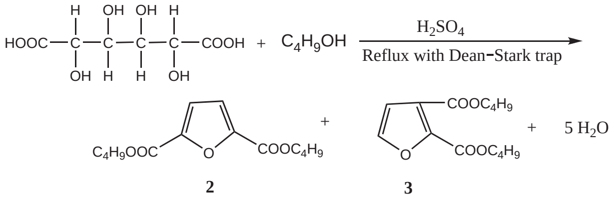
Dibutyl 2,5-furandicarboxylate (**2**) and dibutyl 2,3-furandicarboxylate (**3**) were synthesized using one step from galactaric acid and 1-butanol. Sulfuric acid, *p*-toluenesulfonic acid, and heteropolyacids were good catalysts for the reaction. The reaction time was dependent on the amount of the catalyst, but the final yields of the main product, **2** remained unchanged.

The development of biorefineries has become important because of a perceived future global deficiency of fossil resources. The Department of Energy (DOE) in the United States identified the top 12 building-block chemicals, including 2,5-furandicarboxylic acid (**1**) as targets for biorefineries.[1] The compound **1** has two carboxylic acids in a molecule and is expected to be used to produce polyesters like poly(ethylene terephthalate). It has been reported that **1** could be produced from renewable resources such as galactaric acid,[2,3] furancarboxylic acid,[4] 5-hydroxymethylfurfural,[5–7] and fructose[8,9] derived from saccharide. The synthesis of **1** from galactaric acid seems to be one of the most promising routes because of the availability of resources and the simple reaction conditions. Lewkowski[2] reported the synthesis of **1**, with good yields, from the reaction of galactaric acid and *p*-toluenesulfonic acid. However, the reaction conditions are severe—we could not obtain the target product. In addition, the purification of **1** is not trivial because **1** cannot be distilled and is insoluble in common organic solvents.

In this paper, we wish to report a one-step facile synthesis procedure of dibutyl 2,5-furandicarboxylate (**2**) and dibutyl 2,3-furandicarboxylate (**3**) from the reaction of galactaric acid and 1-butanol in the presence of sulfuric acid (Scheme 1). The purification of **1** and direct polycondensation of **1** with diols are difficult because **1** is infusible and insoluble using ordinary solvents. In contrast, the diester of **1**, dialkyl 2,5-furandicarboxylate, is simple to purify because they can be distilled or recrystallized using existing solvents and can be polymerized directly using diols.[10,11] Although Bratulescu[12] reported the synthesis of dialkyl 2,5-furandicarboxylate from glucaric acid, the process requires the use of extra steps, such as processing using a microwave. A 200-mL flask with a Dean–Stark trap and an air condenser was charged with galactaric acid, 1-butanol, and sulfuric acid. The mixture was refluxed in an oil bath. The mixture was at first a white suspension since all the galactaric acid does not dissolve even in hot 1-butanol. As the reaction progressed the mixture changed to a dark transparent solution. The water generated by the dehydration or esterification of the galactaric acid was distilled and separated out of the solution through the Dean–Stark trap. Finally, the reactant was cooled and poured into 150 mL of diisopropyl ether. The ether extraction was washed with three 100-mL portions of water, 100-mL 1% aqueous NaOH solution, and two 100-mL portions of water. After drying over sodium sulfate the solution was subjected to evaporation. The residue was distilled with a Kugelrohr to produce **2** as the major product. At the same time a small amount of **3** was also obtained. The products **2** and **3** were purified by distillation and recrystallization with methanol and identified with IR, ^{1}H NMR, and ^{13}C NMR.[13,14] To the best of the authors' knowledge no report has been published which discusses the production of 2,3-furandicarboxylic acid using the dehydration of galactaric acid. The structure of **3** was identified based on the twin doublet of furan ring protons in ^{1}H NMR.[14]



Scheme 1.

In Table 1 the yields of **2** and **3** from the reaction of galactaric acid and 1-butanol using sulfuric acid as a catalyst are shown. The reaction did not proceed without the catalyst (Run 1). The reaction, except for Run 1, continued until the solution became homogeneous at room temperature. Although the molar ratio of 1-butanol to galactaric acid varied from 44 (Run 7) to 11 (Run 8), the yields of **2** were found to change by only a small amount. The reaction time was dependant on the amount of sulfuric acid. However, the final yield of **2** was found not to change. The amount of extracted water was about 2–6 mL. A considerable amount of dibutyl sulfate and dibutyl ether were produced as by products (Scheme 2).

Figure 1 is a plot of the yield as a function of reaction times of **2** and **3**, where the reaction was galactaric acid with 1-butanol, using sulfuric acid as the catalyst. Hexadecane was added to the reaction as the reference for the GLC analysis. About 2 mL of the reactant was taken at regular time intervals. After the extraction of the diisopropyl ether the yields of **2** and **3** at that time were

Table 1. The yields of **2** and **3** from the reaction of galactaric acid and 1-butanol

Run	Galactaric acid /g	1-BuOH /mL	H_2SO_4 /g	Time /h	Yield/%	
					2	**3**
1	5.0	50	None	53	0	0
2	5.0	50	0.5	40	53	11
3	5.2	50	1	25	49	12
4	5.0	50	3	19	56	17
5	5.8	50	5	8	54	9
6	5.0	50	10	7	64	4
7	5.0	100	5	13	49	13
8	10.0	50	5	6	46	6

$$C_4H_9OH + H_2SO_4 \longrightarrow (C_4H_9O)_2SO_2 + 2H_2O$$

$$C_4H_9OH \xrightarrow{H_2SO_4} C_4H_9OC_4H_9 + H_2O$$

Scheme 2.

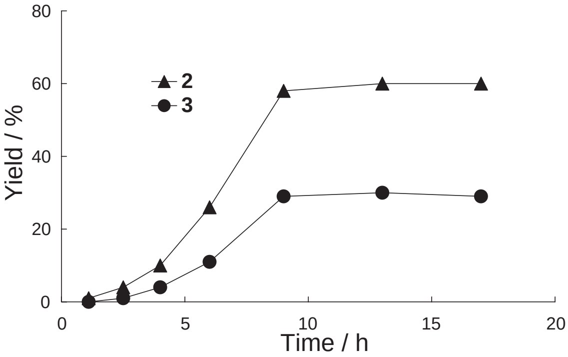


Figure 1. Plots of the yield as a function of the reaction time, for the reaction of galactaric acid with 1-butanol. Reaction conditions: galactaric acid 10.1 g, 1-butanol 100 mL, hexadecane 1.06 g, sulfuric acid 10.0 g.

Table 2. The yields of **2** and **3** from the reaction of galactaric acid with 1-butanol[a]

Run	Catalyst	mmol	Time /h	Yield/% **2**	Yield/% **3**
9	*p*-TsOH	10	26	44	16
10	*p*-TsOH	26	18.5	38	12
11	*p*-TsOH	78	8.3	49	25
12	H_3PO_4	21	40	4	7
13	H_3PO_4	164	8.5	5	7
14	Sc(O-Tf)$_3$	2.1	19	6	5
15	$SiO_2 \cdot 12WO_3 \cdot 26H_2O$	2.4	11	37	12
16	$H_3PW_{12}O_{40} \cdot nH_2O$	2.4	14.5	44	8

[a]Galactaric acid 5.0 g (23.8 mmol), 1-butanol 50 mL, refluxed with Dean–Stark trap.

measured using GLC. It was found that with longer reaction times, up to 9 h, higher yields of **2** and **3** were obtained; the total yield of **2** and **3** reached 90%. GLC analysis showed higher yields of **2** and **3** than those of distillation as in Table 1. It was considered that some amounts of **2** and **3** remained trapped in the distillation residue. At the end of the reaction 16.8 mL (0.93 mol) of water was extracted using azeotrope. Theoretically, 5 mol of water is produced when 1 mol of galactaric acid is transformed to dibutyl furandicarboxylate. This means that 4.3 mL (0.24 mol) of water is produced during the conversion of 10 g (48 mmol) of galactaric acid. The rest of the extracted water (12.5 mL) is formed when dibutyl sulfate and dibutyl ether are produced. Finally, 18.8 g of dibutyl sulfate was found at 17 h from GLC measurements, suggesting that 88% of the sulfuric acid was esterified.

Table 2 presents data that highlights the effect of various catalysts on the reaction of galactaric acid and 1-butanol. *p*-Toluenesulfonic acid was found to be a good catalyst similar to sulfuric acid (Runs 9–11). Although a large amount of *p*-toluenesulfonic acid was used for the conversion of galactaric acid into **1**,[2] a smaller molar ratio of *p*-toluenesulfonic acid than galactaric acid also produced good results (Run 9). Heteropolyacids, such as $SiO_2 \cdot 12WO_3 \cdot 26H_2O$ and $H_3PW_{12}O_{40} \cdot nH_2O$, catalyzed the reaction at a smaller molar ratio compared to sulfuric acid (Runs 15 and 16). Scandium triflate has also been reported to be a good catalyst for esterification.[15] However, it is not as active in this reaction (Run 14). The yield of **3** was found to be dependent on the type and the amount of catalyst.

Future work will look at determining the formation mechanism and the effects of various alcohols and catalysts.

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13 Data for **2**: IR (KBr) 1724 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.97 (t, 6H, $J = 7.4$ Hz, $2CH_3$), 1.45 (hex, 4H, $J = 7.6$ Hz, $2CH_2$), 1.75 (quin, 4H, $J = 7.4$ Hz, $2CH_2$), 4.34 (t, 4H, $J = 6.8$ Hz, $2CH_2$), 7.19 (s, 2H, 2CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.21, 146.95, 118.20, 72.95, 30.63, 19.11, 13.70.
14 Data for **3**: IR (KBr) 1721 cm^{-1}, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.94–0.99 (m, 6H, $2CH_3$), 1.40–1.52 (m, 4H, $2CH_2$), 1.69–1.75 (m, 2H, CH_2), 1.81–1.87 (m, 2H, CH_2), 3.99 (t, 2H, $J = 6.6$ Hz, CH_2), 4.30 (t, 2H, $J = 6.6$ Hz, CH_2), 6.47 (d, 1H, $J = 7.6$ Hz, CH), 7.12 (d, 1H, $J = 7.6$ Hz, CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.56, 156.69, 149.00, 141.10, 111.55, 110.93, 69.60, 65.87, 30.58, 30.48, 19.11.
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