Homogeneous Sn-Catalyzed Transformation of Algal Residue into Important Chemicals

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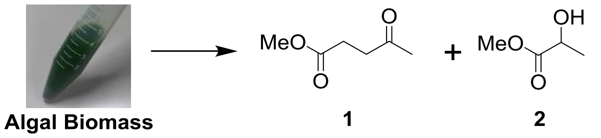
Algal biomass has received attention as an alternative carbon resource owing not only to its high oil production efficiency but also, unlike corn starch, to its lack of demand in foods. However, algal residue is commonly discarded after the abstraction of oil. The utilization of the residue to produce chemicals will therefore increase the value of using algal biomass instead of fossil fuels. Here, we report the use of algal residue as a new carbon resource to produce important chemicals. The application of different homogeneous catalysts led to the selective production of methyl levulinate (**1**) or methyl lactate (**2**).[1]

The preparation of algae as a reaction substrate is described. After the cultivation of algae, centrifugation, freezing, and dehydration steps afforded a green powder containing mineral ions and a pigment extracted with methanol from the cells. Then, the powder was suspended in methanol, and sonication of this mixture provided the reaction substrate in methanol solution. When the sonication is carried out in methanol, the prepared substrate contains both oil and carbohydrates.

Table.1 Conversion of algae into **1** and **2** using $Sn(OTf)_2$ or $SnBr_4$.[a]



Entry	Catalyst	**1** (%)[e]	**2** (%)[e]
1[b]	$Sn(OTf)_2$	0	0
2[c]	$Sn(OTf)_2$	40	8
3[d]	$SnBr_4$	6	33

[a]Reaction conditions: methanol (5.0 mL), catalyst (0.24 mmol), naphthalene (0.156 mmol), Ar (5 atm), 24 h, 160 °C. [b]Catalyst (0.024 mmol). Algae (100 mg) containing 55.5 mg of carbohydrates. [c]Algae (53.4 mg) containing 29.6 mg of carbohydrates. [d]Algae (75.2 mg) containing 38.1 mg of carbohydrates. [e]Yields of **1** and **2** were based on the amount of carbohydrates, and were determined by ^{1}H NMR analysis.

As shown in entry 1 Table 1, when the use of $Sn(OTf)_2$ was applied, the desired products **1** and **2** were not obtained. On the other hand, in the detailed GC-MS analysis, peaks derived from the oil components of algae were observed. This result indicates that the mineral ions and pigment contained in algae influenced the catalytic activity, likely through catalyst poisoning. Therefore, the sample obtained after sonication was filtered, washed with methanol, and then dried i*n vacuo* to remove the mineral ions and pigment. This sample was then used to examine the degradation of the algal carbohydrates. Using $Sn(OTf)_2$, the desired products **1** and **2** were obtained in 40% and 8% yields, respectively (entry 2). The use of $SnBr_4$ was also demonstrated, and **2** was predictably obtained as the major product; that is, **1** and **2** were obtained in 6% and 33% yields, respectively (entry 3). This production yield of **2** is equal to the results of the previous report[2] on the conversion of mono- and disaccharides into alkyl lactates. These results demonstrate the successful development of new carbon resources as a solution for the depletion of fossil fuels.

In this reaction system, **1** and **2** were obtained by the degradation of algae. A glucose monomer is generated through the disconnection of a glycosidic bond in carbohydrates. Then triose sugars are obtained via an isomerization of glucose monomer and a [3+3] retro-aldol reaction, and the conversion of triose sugars into **2** proceeded.[3] When we applied $Sn(OTf)_2$ as a catalyst, **1** was obtained via the dehydration of glucose (cf. entry 2 Table 1). Furthermore, the use of $SnBr_4$ accelerated the [3+3] retro-aldol reaction (cf. entry 3 Table 1). Although this selectivity is obviously dependent on the Lewis acidity of Sn, the reason why the use of $SnBr_4$ selectively produces **2** remains unclear.

REFERENCES

[1] S. Yamaguchi, Y. Kawada, H. Yuge, K. Tanaka and S. Imamura, (2017) submitted.
[2] M. S. Holm, S. Saravanamurugan and E. Taarning, Science, 328 (2010) 602.
[3] Y. Hayashi and Y. Sasaki, Chem. Commun., 41 (2005) 2716.