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Site-Selective Hydrosilylation of Botryococcene - The Algal Biomass Hydrocarbon Oil

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Abstract: An algal acyclic triterpene botryococcene ((*E*)-2,3,7,10,13,16,20,21-octamethyl-6,17-dimethylene-10-vinyldocosa-1,11,21-triene), new biomass for material sources, which has three-types of six carbon-carbon double bonds, *i.e.*, four vinylidenes at C2,6,17,21-positions, one C10-vinyl, and one C11-12 internal olefin, in the molecule underwent hydrosilylation of various organosilanes in the presence of Pt(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst). Various hydrosilylated botryococcene derivatives were site- and regioselectively obtained in high yields by an *anti*-Markovnikov type addition at the C10-vinyl moiety without any isomerizations of the unsaturated triterpenoid skeleton.

Introduction

Botryococcus braunii, a freshwater microalga, produces a variety of acyclic and monocyclic terpene hydrocarbons known as botryococcene. The production efficiency of botryococcene from *B. braunii* is high, and the oil contents are 17-90 w% in the dry alga body,[1] which has accelerated researches on large-scale production of the algae biomass for the utilization of renewable energy and material sources.[2] Among them, M. Watanabe et al. have reported that *B. braunii* (the strain Bot-22) dominantly produces a specific botryococcene (**1**) shown in Figure 1.[3,4]

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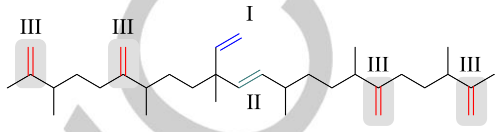


Figure 1. The chemical structure of botryococcene **1**.

Botryococcene **1** has three types of six C-C double bonds of vinyl (I), internal *trans*-olefin (II), and vinylidene (III) in the molecule. Unlike most other biomass sources, **1** has no heteroatoms similar to main structures of petroleum components. From the perspective of syhthetic organic chemistry, **1** should be a target for natural product synthesis because it has a peculiar chemical structure including a quaternary asymmetric carbon. Histrically, botryococcene analogues have been studied in organic chemistry for structural determination and elucidation of biosynthetic pathways,[5,6] and the first total synthesis of **1** was achieved by J. D. White et al. in 1988.[7] However, except for the structure determination, little has been known about reactivity and chemical transformations of **1**. It is necessary to develop methods for selective modifications of **1** to use as a source of chemical materials, because **1** merely has the three types of plural inactive C-C double bonds. It is thought that the reactivity of **1** in common organic reactions is usually low, *i.e.*, (i) the type-I vinyl moiety that positions in the middle of the terpenoid, whose reactivity should be suppressed by steirc suroundings, (ii) the type-II internal olefin between the tertially and quaternary carbons was specifically unreactive due to the buried environment, and (iii) the reactivity of the type-III four vinylidene moieties should be identical to that of similar terpenoids.[8]

It is envisaged that hydrosilylation of **1** with hydrosilanes can proceed by selecting an appropriate transition metal catalyst, because inactive alkenes and alkynes have been reported to react with various hydrosilanes when the certain catalyst was used such as Pt, Ru, Rh, Fe, Co and Ni.[9-12] In particular, the Pt-based catalysts showing high reactivity have been extensively studied and used industrially. Furthermore, a site-selective reaction for **1** is expected to proceed, because terminal olefins should preferentially undergo hydrosilylation compared to branched olefins.[13]

In this paper, it is reported that a series of botryococcene derivatives are succesfully synthesized in high yields by a site-selective hydrosilylation of **1** with various organosilanes using a Pt-based catalyst. The selective modification of **1** can indicate applicability of the algal substance to chemical materials.

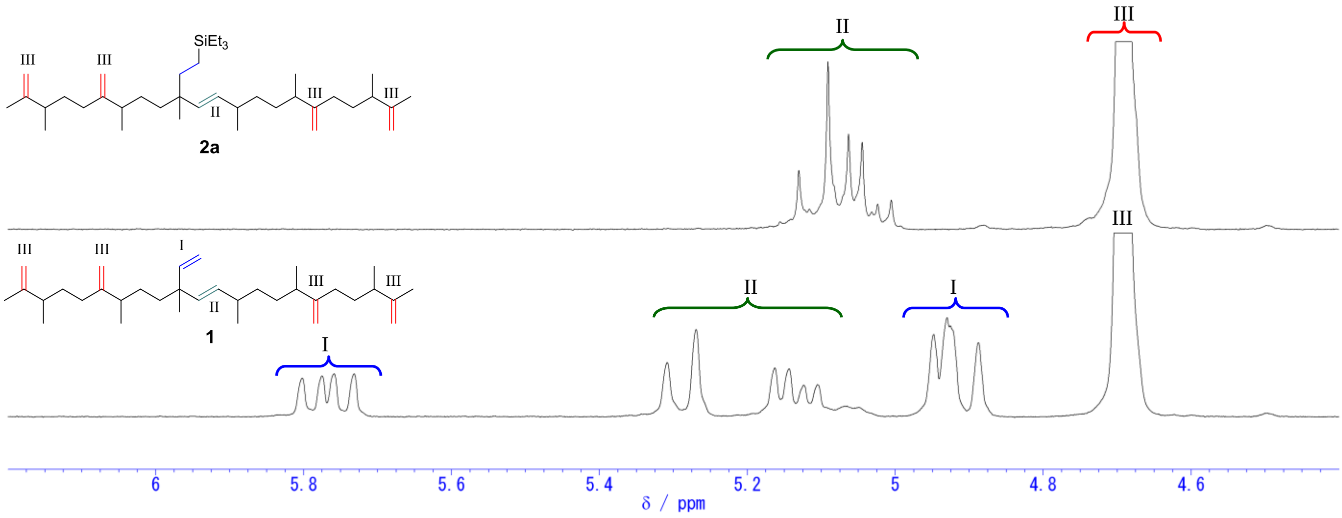


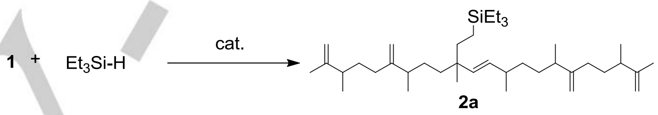
Figure 2. The ^{1}H NMR spectra of botryococcene **1** and the hydrosilylated product **2a**.

Results and Discussion

First, to clarify the reactivity of **1** for hydrosilylation, **1** was reacted with Et_3SiH in the presence of various Pt-catalysts (Table 1). The hydrosilylation of **1** (0.2 mmol, 1 equiv.) with Et_3SiH (2 equiv.) was carried out in 2-propanol (1 mL) at 80 °C for 24 h in the presence of $PtCl_2$ (1 mol%) under an Ar atmosphere in a homogeneous system (entry 1). The products were analyzed by ^{1}H NMR. The isolated dominant product was a monohydrosilylated botryococcene derivative at the C10 vinyl moiety (**2a**) as shown in the reaction formula in Table 1, which was identified by characteristic signals (0.31–0.39 (multiplet (m), 2 H) ppm) for CH_2 adjacent to the inserted $SiEt_3$ moiety (see electronic supplementary information) in addition to the change of characteristic alkene signals of **1** and **2a** in the area of 4.7–5.8 ppm. In the presence of $PtCl_2$, the conversion of **1** was 75% while **2a** was dominantly produced in 8% yield. The yields and conversions were determined by ^{1}H NMR analyses using 1,1,2-trichloroethane as an internal standard. The criteria ^{1}H NMR signals of 1,1,2-trichloroethane at 4.0 (doublet(d), 2 H) and 5.8 (triplet(t), 1 H) ppm did not overlap all the signals of **1** (0.9–2.2, 4.7–5.76 ppm) and **2a** (0.3–0.55, 0.8–2.2, 4.7–5.2 ppm) (see electronic supplementary information).

Comparing the ^{1}H NMR spectra between **1** and the isolated **2a** in detail, it is revealed that the hydrosilylation of **1** with Et_3SiH proceeds with high site-selectivity. The ^{1}H NMR spectra of **1** and **2a** in the area of 4.4–6.2 ppm for the olefinic protons were shown in Figure 2. The ^{1}H NMR signals for the type-I vinyl moiety of **1** observed at 4.91 (d, 1 H), 4.94 (d, 1 H) and 5.77 (dd, 1 H) ppm completely dissapeared from the spectrum of **2a**. On the other hand, the signals for the type-II internal olefin of **2a** were observed in the region of 5.0–5.1 (d and dd, 2 H) ppm. The ^{1}H NMR signals of internal olefin were shifted from 5.1–5.3 ppm of **1** to 5.0–5.1 ppm of **2a**, because the protons of the internal olefin of **2a** were shielded by the C10-(triethylsilyl)ethyl moiety. It was suggested that the type-I vinyl is fully consumed by the hydrosilylation.

Table 1. Hydrosilylation of botryococcene **1** with Et_3SiH. [a]



entry	catalyst	solvent	yield of **2a** /%[b]	conv. of **1** /%[b]
1	$PtCl_2$	2-propanol	8	75
2	$H_2PtCl_6/6H_2O$	2-propanol	<1	21
3	$Pt(NH_3)_4(NO_3)_2$	2-propanol	7	23
4	*trans*-$Pt(NH_3)_2Cl_2$	2-propanol	43	>99
5	$[(C_6H_5)_3P]_2Pt(H_2C=CH_2)$	2-propanol	53	89
6	Karstedt's catalyst	2-propanol	63	>99
7	Karstedt's catalyst	toluene	89	92
8	Karstedt's catalyst	THF	91	>99
9	Karstedt's catalyst	$ClCH_2CH_2Cl$	91	>99
10	Karstedt's catalyst	none	91	>99

[a] Conditions: [**1**] = 0.2 mol dm^{-3}, [Et_3SiH] = 0.4 mol dm^{-3} (2 eq), [catalyst] = 0.002 mol dm^{-3} (1 mol%) , in solvent (1 mL) at 80 °C for 24 h under Ar. [b] The yields and conversions were determined by ^{1}H NMR.

The signals of the type-III four vinylidene moieties of **1** and **2a** were observed at 4.69 (singlet(s), 8 H) and did not change after the hydrosilylation. In addition, it has been known that the Pt catalyzed hydrosilylation of several branched olefins such as 2-hexene and 3-hexene frequently gives unordinary adducts through isomerization of the olefins to more reactive terminal ones such as 1-hexene.[14] In the case of hydrosilylation of **1**, the reaction site-selectively proceeded only at the vinyl moiety (type-I) without detection of isomerized products, although **1** has a branched structure involving the type-II and type-III carbon-carbon double bonds in the molecule. The reason is because the internal *trans*-olefin and four vinylidene moieties that are inactive to the hydrosilylation do not isomerize into reactive terminal vinyl moieties. In summary, the appearance of CH_2 signals at 0.31–0.39 ppm after addition of Et_3SiH at the vinyl moiety (I) , the change of the olefinic protons' signals between **1** and **2a**, and little detection of byproducts signals can elucidate that hydrosilylation of **1** proceeded with high site- and regioselectivity at the type-I vinyl moiety.

When $H_2PtCl_6/6H_2O$ (Speier's catalyst), an effective hydrosilylation catalyst,[9] was used instead of $PtCl_2$ (entry 2), the reaction was retarded, resulting in the lower conversion of **1** and little production of **2a** under the same conditions. Similarly, $Pt(NH_3)_4(NO_3)_2$ was also not effective, showing low conversion of **1** (entry 3). The use of a divalent amine coordinated Pt catalyst, *trans*-$Pt(NH_3)_2Cl_2$,[15] enhanced the reactivity of **1** in large in the conversion of **1** (>99%) and production of **2a** (43% yield) (entry 4). More effective to increase yield of **2a** was using Pt catalysts with π-ligands, such as $[(C_6H_5)_3P]_2Pt(H_2C{=}CH_2)$[16] and Karstedt's catalyst (Pt(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex)[10,17,18] (entries 5 and 6). However, a variety of unidentified minor products were detected in all cases, which might be due to competitive formations against **2a** and presence of impurities in **1**.

The difference in reactivity of each catalyst observed in Table 1 is considered from the viewpoint of activity in each catalytic process based on the proposed mechanism.[19,20] As shown in Figure 3, the Pt catalyst with ligands (Ln) (**A**) undergoes oxidative addition of hydrosilane (H-SiR_3), giving a reactive species (**B**) as usual, which must coordinate **1** rapidly to give species (**C**) for progress of the catalysis cycle. However, the formation step of **C** by coordinating **1** with **B** is a rate determining step due to large steric hindrance of **1** in the reactive type-I vinyl site vicinal to the quaternary **C** in **1**. Consequently, conversion of **1** should fall to a low level when the ligand exchange velocity is slow, because the confined **B** should be destined for inactivation such as degradation to metal.[19] Meanwhile, in order for hydrosilylation to proceed efficiently, at least the L in the species **B** must promptly be exchanged with botryococcene **1**.

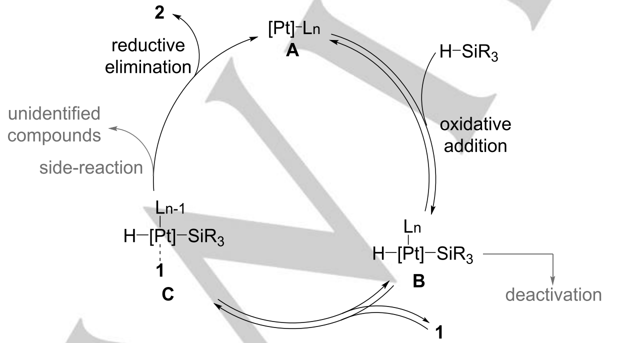


Figure 3. The supposed catalytic hydrosilylation cycle of **1**.

In the case of $PtCl_2$ (entry 1), the coordination of the sterically hindered large molecule **1** to **B** proceeds smoothly, as it has no intended ligands. However, the octahedral complexes fully coordinated with valid ligands would not smoothly proceed the ligand exchange with **1**, resulting in the considerable low conversions (entries 2 and 3). On the other hand, there is room for coordination of **1** for the square-planar complex, *trans*-$Pt(NH_3)_2Cl_2$, attaining the high conversion (entry 4). The catalysts having π-ligands are also proper, because the π-ligands must be easily exchangeable with **1** (entry 5 and 6). In particular, the Karstedt's catalyst has a merit to stabilize **B** by the bidentate non-rigid π-ligand. After the ligand exchange of **B** with **1**, reductive elimination of the species **C** should give **2**, and this process is key to determine the reaction selectivity as well as production yield of **2**. Activation and stabilization on **C** that is coordinated with **1** at the site of type-I vinyl must be important factors to give **2** in high yields with few byproducts, since several side reactions such as dehydrogenative sillylation and olefin hydrogenation, have been recognized.[10] The Karstedt's catalyst worked most effectively in this step too (entry 6).

Next, solvent effect was examined to improve the production yield of **2a**. 2-Propanol which has been generally used in hydrosilylation[9] was changed to another solvent under the same conditions of entry 6 using the Karstedt's catalyst. When toluene was used as the solvent, the yield increased but the conversion somewhat decreased (entry 7). The efficient production of **2a** in 91% yields and completion of conversions were attained in THF (entry 8), in 1,2-dichloroethane (entry 9), and under solvent-free conditions (entry 10). These results suggest that less donor environment than that in the isopropanol solvent is preferable to hold activity of **C** for progress of the selective hydrosilylation.

Lastly, the various organosilanes were applied to react with **1** under the best conditions of entry 9 in 1,2-dichloroethane, and the structures of hydrosilylated products **2** and their high production yields determined by ^{1}H NMR were shown in Figure 4. Triethoxysilane efficiently reacted with **1**, and **2b** was isolated in 78% yield. $(PhCH_2)_3SiH$ and Ph_3SiH that have aromatic rings also site-selectively reacted well with **1**, giving **2c** and **2d** in 84% and 77% isolated yields, respectively. Interestingly, **1** did not react with *i*Pr_3SiH at all. This suggests that the reactive vinyl site of **1** was difficult to access to the more sterically hindered *i*Pr_3Si linked **B** compared with the other R_3Si linked **B**.

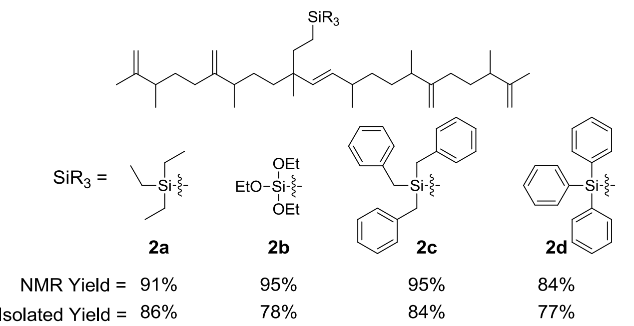


Figure 4. Hydrosilylated botryococcenes **2**.

Conclusions

It was found that botryococcene **1**, an unsaturated hydrocarbon ($C_{34}H_{58}$) produced from *Botryococcus braunii* (Bot-22), could quantitatively be modified to a monohydrosilylated derivative **2**. This is the first report that **1** was selectively converted to a botryococcene derivative as an isolable and dominant product. Difficulty against selective modifications of **1** is that **1** has three types of plural carbon-carbon double bonds, *i.e.*, a vinyl (I), an internal *trans*-olefin (II), and four vinylidene moieties (III), in the molecule. Since hydrosilylation has usually been applied to terminal olefins to produce *anti*-Markovnikov addition alkanes in good yields, hydrosilylation of **1** with an organosilane was investigated in the presence of a Pt catalyst, for the first time. Unexpectedly, **1** showed low reactivity under general conditions for the hydrosilylation reactions. After optimization, the hydrosilylation of **1** proceeded in high yields with high site- and regioselectivity at the reactive vinyl moiety (I) without isomerizations in the low-donor environment using the Karstedt's catalyst. It is demonstrated that various organosilanes could be applied to this reaction, which suggests that the terpenoid moiety of **1** can be embedded in materials via a silylene linkage to add functionality such as bioactivity, lubricity, and cross-link activity. Moreover, these results provide the potential for biomass utilization of algal productions in chemical industry.

Supporting Information Summary

Experimental Section associated with this article can be found in electrical supporting information.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Algae biomass hydrocarbon oil • Biomass • Botryococcene • Hydrosilylation • Siteselective reaction

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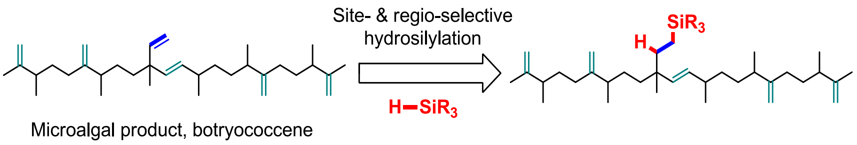

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