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

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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 interpenon 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 algal 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]

![Botryococcene 1](image)

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 synthetic organic chemistry, 1 should be a target for natural product synthesis because it has a peculiar chemical structure including a quaternary asymmetric carbon. Historically, botryococcene analogues have been studied and used industrially. Furthermore, a site-selective modification of 1 using Pt-based catalyst. The selective modification 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.
Results and Discussion

First, to clarify the reactivity of 1 for hydrosilylation, 1 was reacted with Et3SiH in the presence of various Pt-catalysts (Table 1). The hydrosilylation of 1 (0.2 mmol, 1 equiv.) with Et3SiH (2 equiv.) was carried out in 2-propanol (1 mL) at 80 °C for 24 h in the presence of PtCl2 (1 mol%) under an Ar atmosphere in a homogeneous system (entry 1). The products were analyzed by ¹H 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 CH2 adjacent to the inserted SiEt3 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 PtCl2, the conversion of 1 was 75%, while 2a was dominantly produced in 8% yield. The yields and conversions were determined by ¹H NMR analyses using 1,1,2-trichloroethane as an internal standard. The criteria ¹H 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 ¹H NMR spectra between 1 and the isolated 2a in detail, it is revealed that the hydrosilylation of 1 with Et3SiH proceeds with high site selectivity. The ¹H 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 ¹H 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 ¹H 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.

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. In the case of hydrosilylation of 1, the

![Figure 2. The ¹H NMR spectra of botryococcene 1 and the hydrosilylated product 2a.](image-url)

| Table 1. Hydrosilylation of botryococcene 1 with Et₃SiH. |  |
|---|---|---|---|
| entry | catalyst | solvent | yield of 2a [%] | conv. of 1 [%] |
| 1 | PtCl₂ | 2-propanol | 8 | 75 |
| 2 | H₂PtCl₆/B₆H₆O | 2-propanol | <1 | 21 |
| 3 | Pt(NH₃)₄(ONO)₂ | 2-propanol | 7 | 23 |
| 4 | trans-Pt(NH₃)₂Cl₂ | 2-propanol | 43 | >99 |
| 5 | (C₆H₅)₂P₂Pt(H₂C=CH₂) | 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 | CICH₂CH₂Cl | 91 | >99 |
| 10 | Karstedt’s catalyst | none | 91 | >99 |

[a] Conditions: [I] = 0.2 mol dm⁻³, [Et₃SiH] = 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 ¹H NMR.
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 CH2 signals at 0.31–0.39 ppm after addition of Et3SiH 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 H2PtCl6/6H2O (Speier’s catalyst), an effective hydrosilylation catalyst,[9] was used instead of PtCl2 (entry 2), the reaction was retarded, resulting in the lower conversion of 1 and little production of 2a under the same conditions. Similarly, Pt(NH3)2(NO3)2 was also not effective, showing low conversion of 1 (entry 3). The use of a divalent amine coordinated Pt catalyst, trans-Pt(NH3)2Cl2[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 τ-ligands, such as [(C6H5)3P]2Pt(H2C=C=CH2) 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-SiR3), 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 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.[21]

Meanwhile, in order for hydrosilylation to proceed efficiently, at least the L in the species B must promptly be exchanged with botryococcene 1.

In the case of PtCl2 (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(NH3)2Cl2, attaining the high conversion (entry 4). The catalysts having τ-ligands are also proper, because the τ-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 τ-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 silylation 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 conversion 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 1H NMR were shown in Figure 4. Triethoxysilane efficiently reacted with 1, and 2b was isolated in 78% yield. (PhCH3)3SiH and Ph3SiH 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 Pr3SiH at all. This suggests that the reactive vinyl site of 1 was difficult to access to the more sterically hindered Pr3Si linked B compared with the other R3Si linked B.

[Figure 3. The supposed catalytic hydrosilylation cycle of 1.](image)

[Figure 4. Hydrosilylated botryococenes 2.](image)
Conclusions

It was found that botryococcene 1, an unsaturated hydrocarbon \( \text{C}_{30}\text{H}_{50} \) produced from \textit{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 • Site-selective reaction

[2] For industrial applications of algae research, we (Algae Biomass and Energy System R&D Center in University of Tsukuba) are promoting to develop an algae-based renewable energy and material source production system.
An unsaturated hydrocarbon biomass (C_{34}H_{58}) produced from *Botryococcus braunii* (a freshwater microalga), could quantitatively be modified to a monohydrosilylated derivatives with high site- and regio selectivity.