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Research Article

Selective Synthesis of Glycerol Monostearate by Glycerol Borate

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Abstract

Glycerol monostearate, a widely used nonionic surfactant in food, pharmaceutical, and cosmetic industries. However, current synthesis methods such as molecular distillation and functional group protection suffer from high equipment costs, complex post-processing, or low product purity. In this study, a boric acid ester protection method was developed to selectively synthesize high-purity glycerol monostearate. Quantum chemical calculations (AM1 method) and Monte Carlo simulations were used to predict optimal reaction conditions. Bisglyceride borate was synthesized and characterized by FT-IR, then esterified with stearic acid, and hydrolyzed to yield the final product. The optimal conditions were: glycerol-to-boric acid molar ratio 2:1, 115 °C with toluene as azeotropic agent, 70 min (bisglyceride borate conversion: 96.0%). The final product purity was >95% by HPLC, with melting point 61–63 °C and HLB value 3.8. This method offers mild conditions, simple post-processing, and high purity, making it industrially promising.

Keywords: Glycerol monostearate; Boric acid ester protection; Quantum chemical calculation; Monte Carlo simulation; HPLC; FT-IR spectroscopy

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1. Introduction

Food emulsifiers are critical for improving food quality and are a key focus of the light industry [1-3]. Glycerol monostearate (also called monostearin) is a white or pale yellow waxy solid with no odor or taste. It is soluble in ethanol, acetone, and oils but insoluble in water, with a molecular weight of 358.56 and a melting point of 56 °C. Its molecule contains two hydrophilic hydroxyl groups (-OH) and one lipophilic long-chain ester group (-COO-$C_{17}H_{35}$), giving it strong emulsifying capacity. Its HLB value is 3.8 [4], classifying it as a water-in-oil (W/O) emulsifier. Structurally, glycerol monostearate exists in α- and *β*-isomers (Figure 1).

Glycerol monostearate is a versatile nonionic surfactant used as an emulsifier, antifoaming agent, and stabilizer in the food industry. In the food industry, glycerol monostearate is fully degraded into fatty acids and glycerol during human digestion, which are either absorbed or excreted without health risks. It does not affect food taste and is recognized as a safe, environmentally friendly additive, accounting for over 40% of global food emulsifier production.

Glycerol monostearate was first synthesized via direct esterification of stearic acid and glycerol in 1853. Industrial production began in 1929, yielding a mixture of mono-, di-, and triglycerides;

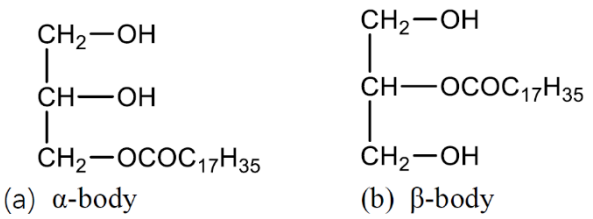

Figure 1. Chemical structures of (a) α-glycerol monostearate and (b) *β*-glycerol monostearate.

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high-purity (>90%) glycerol monostearate was first prepared via molecular distillation in 1943. Current synthesis methods for high-purity glycerol monostearate (>90%) include molecular distillation, functional group protection, and biochemical methods [5-7].

The boric acid ester protection method for glycerol monostearate synthesis has been known in principle, but several critical gaps remain unaddressed: (1) Lack of systematic investigation on reaction conditions for selectively protecting two hydroxyl groups of glycerol via boric acid esterification; (2) Absence of quantitative evaluation of esterification reactivity between different boric glyceride structures and stearic acid; (3) No established optimization strategy for high-purity (>95%) glycerol monostearate production using this method. Novelty of this study: (1) This is the first application of quantum chemical calculations (AM1 method) to elucidate the esterification mechanism between boric acid and glycerol, revealing that intramolecular esterification is thermodynamically more favorable than intermolecular pathways; (2) Monte Carlo simulations are first employed to predict optimal conditions for selective hydroxyl protection, reducing trial-and-error experimentation; (3) Complete experimental validation of computational predictions is provided, establishing a reliable synthesis protocol; (4) The method achieves >95% purity without molecular distillation, significantly simplifying industrial production and reducing equipment costs. The present study aims to (1) elucidate the reaction mechanism and predict optimal conditions for selective hydroxyl protection via quantum chemical calculations and Monte Carlo simulations; (2) experimentally validate the predicted conditions and synthesize high-purity glycerol monostearate; (3) compare the product properties with literature data and commercial standards to confirm the efficacy of the proposed method.

2. Materials and Methods

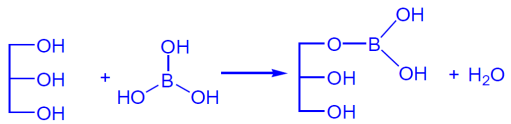
2.1. Quantum Chemical Calculations of Boric Acid-Glycerol Esterification

2.1.1. Reaction equations and calculation methods

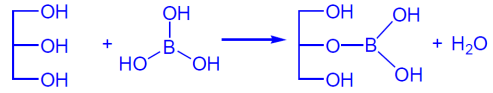
Boric acid (trivalent) and glycerol (with primary α-OH and secondary β-OH) form various borate esters via intermolecular and intramolecular esterification. The main reactions are listed below:

- Intermolecular esterification

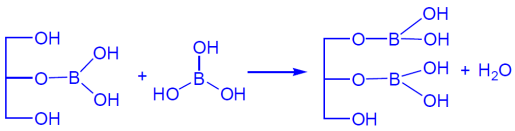
Hydroxyl group of boric acid and hydroxyl of glycerol (glyceride):



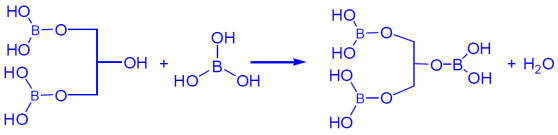
1-boric glyceride (1)



2-boric glyceride (2)

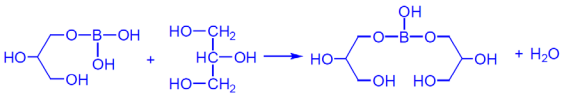


1,2-boric diglyceride (3)

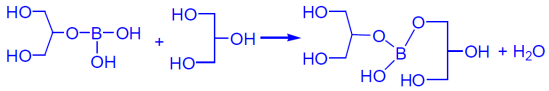


1,2,3-boric triglyceride (4)

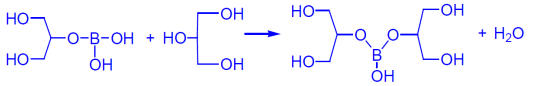
Bifunctional hydroxyl groups of glycerides and hydroxyl groups of glycerin (glycerides):



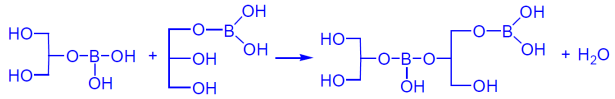
1,1'-bis-borate glyceride (5)



2,1'-bis-borate glyceride (6)

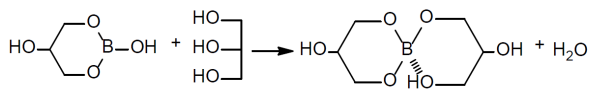


2,2' -bis-boric acid glyceride (7)

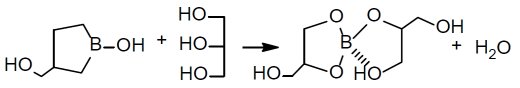


2,2'-bis-boric acid diglyceride (8)

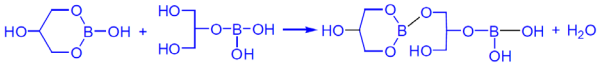
Boronic acid monofunctional hydroxyl of glycerides and hydroxyl of glycerin (glycerides):



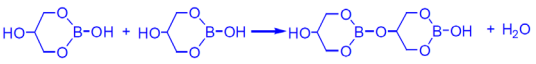
1,3-1',3'-bisglyceride borate (9)



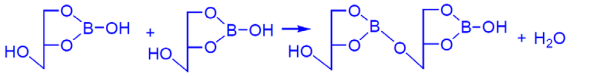
2,1-1',2'-bisglyceride borate (10)



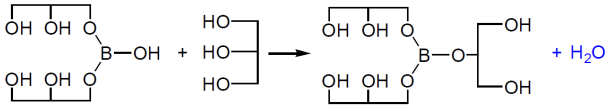
1,3-1',2'-bis-boric acid diglyceride intermolecular ester (11)



1,3- boric acid glyceride intermolecular ester (12)



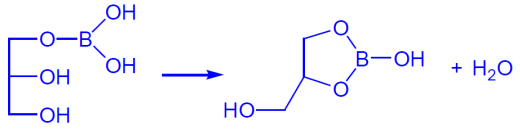
1,2- boric acid glyceride intermolecular ester (13)



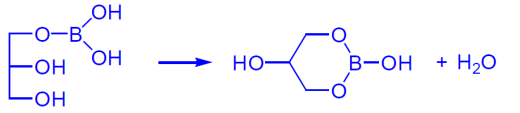
tri-borate glyceride (14)

- Intramolecular esterification

Hydroxyl group of glycerides and hydroxyl group of boric acid bifunctional:

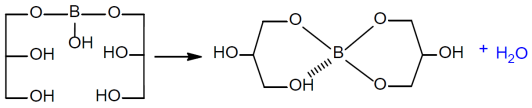


1,2-monoborate glyceride (15)

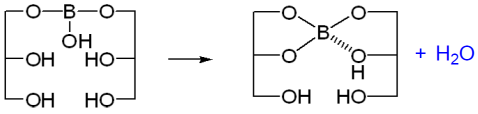


1,3-monoborate glyceride (16)

Hydroxyl group of glyceride and boric acid 1-functional hydroxyl group:

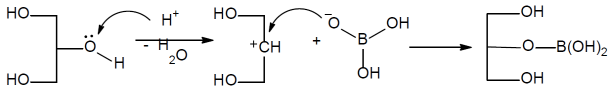


1,1'-3,3'-boric acid bisglyceride (17)



1,1'-2,2-boric acid glyceride (18)

The AM1 method in WinMOPAC2.0 was used to explore transition states (TS) of ester bond formation. Saddle points along the minimum energy path were identified, and TS were verified via vibrational analysis (unique negative frequency) and intrinsic reaction coordinate (IRC) calculations. Activation energy was calculated as the energy difference between the TS and the initial reactant system. For the transient detection of the boronic acid ester formation reaction, the following mechanism is adopted.



(19)

2.1.2. Calculation results and analysis

Tables 1 to 4 summarize the energy changes for different esterification reactions:

- Intermolecular Esterification (Table1, Table 2, Table 3).
- Intramolecular Esterification (Table 4).

These results indicate that the molar ratio of boric acid to glycerol and reaction temperature

Table 1. Energy change of intermolecular esterification reaction between hydroxyl groups of boric acid and hydroxyl groups of glycerol (glycerides) (kJ/mol).

Product	Starting System	Transient State	Generation System	Activation Energy
1-boric acid glyceride	-1 749.2	-1 416.3	-1 694.6	332.9
2-boric acid glyceride	-1 747.2	-1 420.1	-1 692.2	326.9
1, 2-borate diglyceride	-2 451.8	-2 089.0	-2 417.9	362.8
1,2,3-borate triglyceride	-3 184.3	-2 806.8	-3 150.2	377.5

Table 2. Energy change of intermolecular esterification reaction between hydroxyl groups of glycerol and difunctional hydroxyl groups of glycerides (kJ/mol).

Product	Starting System	Transient State	Generation System	Activation Energy
1-1'-glyceride borate	-2 116.5	-1 749.8	-2 087.8	366.7
2-1'-glyceride borate	-2 141.1	-1 769.1	-2 099.2	372.0
2-2'-borate diglyceride	-2 148.1	-1 775.8	-2 063.1	372.3
B(OH)2-G(OH)2	-2 573.6	-2 201.5	-2 501.0	372.1
B(OH)2-G(OH)1	-2 557.2	-2 173.6	-2 520.8	383.6

significantly influence the product distribution, with competitive formation of mono-, di-, and bis-boric glycerides. To selectively protect two hydroxyl groups of glycerol, reaction conditions must be controlled to ensure only one hydroxyl group remains free.

2.2. Monte Carlo Simulation of Boric Acid-Glycerol Esterification

2.2.1. Simulation methods and assumptions

The esterification reaction between boric acid (B-OH) and glycerol (G-OH) can be simplified as:

$$G\text{-}O\text{-}H + B\text{-}O'H = G\text{-}O'\text{-}B + H2O \quad (20)$$

Assumptions: (a) Hydroxyl groups of the same type (e.g., α-OH in glycerol, acidic -OH in boric acid) have identical reactivity; (b) Generated water is immediately removed, avoiding ester hydrolysis; (c) 11 distinct ester bond formation modes are considered, based on the type of hydroxyl groups (boric acid: $B(OH)_3$, $B(OH)_2$, B(OH); glycerol: $G(OH)_3$, $G(OH)_2$, G(OH)); (d) The probability of each reaction mode is determined by its relative rate.

2.2.2. Simulation algorithm

Simulation algorithm includes: (a) Classify acidic hydroxyl groups in the system and select a reactant (e.g., boric acid, boric glyceride) via random sampling based on reactivity probabilities; (b) Check for intramolecular reaction potential; if feasible, proceed with intramolecular esterification; (c) If no intramolecular reaction is possible, select a second reactant (e.g., glycerol, glyceride) with free alcoholic hydroxyl groups; (d). Determine if the reaction proceeds via random number generation (based on relative reaction rates); (e). Update molecular structures and repeat until no free hydroxyl groups remain.

Table 3. Energy change of intermolecular esterification reaction between hydroxyl groups of glycerol and boric acid monofunctional hydroxyl groups of glycerides (kJ/mol).

Product	Starting System	Transient State	Generation System	Activation Energy
1-3-1'-3'-glyceride borate	-1 816.6	-1 478.4	-1 785.6	338.2
2-1-1'-2'-glyceride borate	-1 832.6	-1 497.8	-1 800.3	334.8
triglyceride borate	-2 491.2	-2 154.6	-2 477.2	336.6
B(OH)1-G(OH)2	-2 558.2	-2 215.7	-2 510.9	342.5
1-3- borate glyceride intermolecular ester	-2 256.0	-1 886.9	-2 266.6	369.1
1-2- borate glyceride intermolecular ester	-2 250.1	-1 882.1	-2 253.2	368.0

Table 4. Energy change of the intramolecular esterification reaction (kJ/mol).

Product	Starting System	Transient State	Generation System	Activation Energy
1-3-glyceride borate	-1 420.5	-1 078.3	-1 375.9	342.2
2-1-glyceride borate	-1 418.8	-1 085.5	-1 380.7	333.3
1-1'-3-3'-glyceride borate	-1 817.6	-1 452.5	-1 785.8	365.1
1-1'-2-2'-lyceride borate	-1 826.3	-1 461.6	-1 787.0	364.8

Table 5. Composition of products with glycerol-to-boric acid molar ratio.

Molar Ratio (glycerol-to-boric acid)	After reaction, boric acid content (%)	After reaction, glycerin content (%)	Diglyceride content (%)	Bisglyceride content (%)	Dimeric content (%)	Protective glyceride content (%)	Side reaction product content (%)
1.0	5.5	0.0	85.4	5.5	3.6	88.4	6.8
1.2	1.0	0.0	76.2	20.5	2.2	90.2	6.3
1.4	0.0	0.0	56.8	41.1	2.2	94.6	4.3
1.6	0.0	0.0	39.2	58.8	2.0	97.0	2.3
1.8	0.0	0.5	22.2	75.6	1.7	97.8	2.0
2.0	0.0	0.8	4.6	92.9	0.8	100.0	0.0
2.2	0.0	2.0	3.2	90.6	2.3	97.2	2.5

2.2.3. Simulation results and analysis

- Effect of Glycerol-to-Boric Acid Molar Ratio:
Simulations were run with 1000 boric acid molecules, 100,000 steps, 140 °C, and varying glycerol-to-boric acid molar ratios (1.0–2.2). Results are shown in Table 5 and Figure 2. As the molar ratio increases, the content of diglyceride borate (B-G) decreases, while bisglyceride borate (G-B-G) increases. At a molar ratio of 2.0, the content of "protective glycerides" (glycerol units with two protected hydroxyl groups) reaches 100%, with no side products (glycerol units with all three hydroxyl groups protected). Also, unreacted glycerol content is only 0.8%, minimizing subsequent formation of di- and triglycerides.
- Effect of Reaction Temperature:
Simulations were run with a molar ratio of 2.0, 1000 boric acid molecules, 100,000 steps, and temperatures of 100–200 °C. Results are shown in Table 6 and Figures 3 and 4. As temperature increases, the content of protective glycerides decreases (100% at 100 °C vs. 98.3% at 200 °C), while side product content increases (0% at 100 °C vs. 1.7% at 200 °C). Lower temperatures favor selective protection of two hydroxyl groups, as high temperatures promote side reactions (e.g., triester formation).

2.3. Esterification Reactivity of Boric Glycerides with Stearic Acid

The esterification of boric glycerides with stearic acid follows the acid-catalyzed mechanism, with the rate-limiting step being the formation of a tetrahedral intermediate. Quantum chemical calculations were used to compare the activation energy of this step for different boric glyceride structures (diglyceride borate: B-G; bisglyceride borate: G-B-G; dimer: B-G-B-G).

Results (Table 7) show that the activation energies of the rate-limiting step for different boric glycerides range from 171.5 to 214.6 kJ/mol, with no significant differences. This indicates that all boric glyceride structures exhibit similar reactivity with stearic acid under acid-catalyzed conditions.

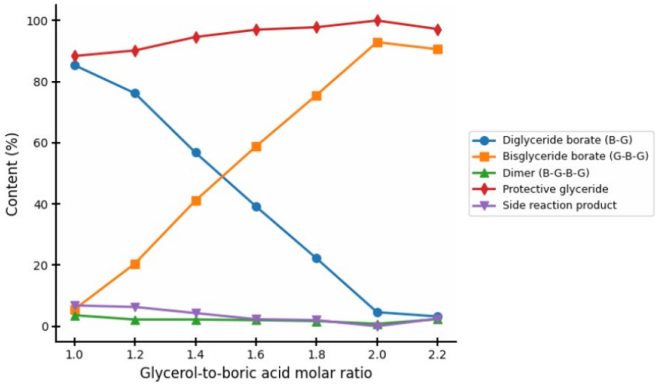


Figure 2. Compositional distribution of products with glycerol-to-boric acid molar ratio.

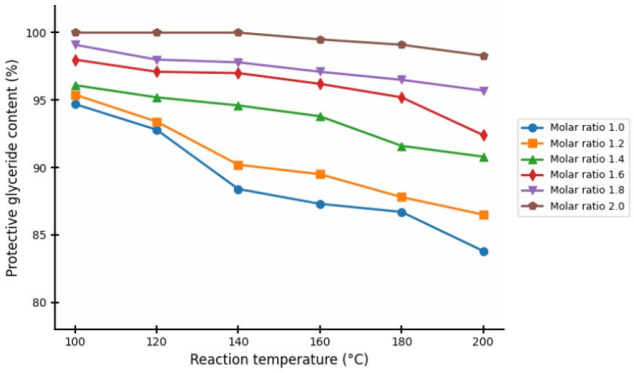


Figure 3. Change in the content of protective glycerides with reaction temperature and molar ratio.

Table 6. Changes in the contents of protective glycerides and side products with temperature at different molar ratios.

Reaction Temperature, ℃	Molar ratio / Division	1.0	1.2	1.4	1.6	1.8	2.0
100	protective glyceride	94.7	95.4	96.1	98.0	99.1	100.0
	side reaction product	3.4	2.9	3.4	1.9	0.9	0.0
120	protective glyceride	92.8	93.4	95.2	97.1	98.0	100.0
	side reaction product	4.7	4.5	3.7	2.4	1.3	0.0
140	protective glyceride	88.4	90.2	94.6	97.0	97.8	100.0
	side reaction product	6.8	6.3	4.3	2.9	2.0	0.0
160	protective glyceride	87.3	89.5	93.8	96.2	97.1	99.5
	side reaction product	7.7	6.6	5.1	3.4	2.8	0.5
180	protective glyceride	86.7	87.8	91.6	95.2	96.5	99.1
	side reaction product	8.5	7.8	7.3	4.3	3.5	0.9
200	protective glyceride	83.8	86.5	90.8	92.4	95.7	98.3
	side reaction product	10.9	9.3	8.1	7.1	4.3	1.7

3. Results and Discussions

3.1. Relationship to Research Objectives and Overview of Findings

The primary objective of this study was to develop a selective, high-purity synthesis method for glycerol monostearate using boric acid ester protection, guided by computational predictions and validated experimentally. The results demonstrate that this objective was successfully achieved through three sequential stages: (1) theoretical prediction of optimal conditions via quantum chemical calculations and Monte Carlo simulations, (2) experimental synthesis and optimization of bisglyceride borate and its stearate ester, and (3) hydrolysis to yield glycerol monostearate with >95% purity.

The key findings are: (1) intramolecular esterification of boric glycerides is thermodynamically more favorable than intermolecular pathways, as revealed by AM1 calculations; (2) Monte Carlo simulations predicted that a glycerol-to-boric acid molar ratio of 2:1 at 115 °C (with toluene) yields 100% protective glycerides with minimal side products; (3) experimental validation confirmed 96.0% conversion for bisglyceride borate synthesis and 98.0% conversion for the subsequent esterification with stearic acid; (4) the final hydrolysis product exhibited 95.15% purity by HPLC, with physical and spectroscopic properties consistent with standard glycerol monostearate.

3.2. Scientific Interpretation of Quantum Chemical Calculation Results

The AM1 calculations (Tables 1–4) provide fundamental insight into the esterification mechanism between boric acid and glycerol. The activation energies for intermolecular esterification range from 326.9 to 383.6 kJ/mol, while intramolecular esterification exhibits activation energies of 333.3–365.1 kJ/mol. Although the absolute values are comparable, the intramolecular pathway is entropically favored because it does not require molecular collision between two separate reactants. This thermodynamic preference for intramolecular cyclization is consistent with well-established principles in organic chemistry, where ring-closing reactions are generally favored over intermolecular condensations when geometrically feasible [8,9].

The lower activation energy for 2-boric glyceride formation (326.9 kJ/mol) compared to 1-boric glyceride (332.9 kJ/mol) suggests that the secondary hydroxyl group (β-OH) of glycerol is slightly more reactive toward boric acid than the primary hydroxyl group (α-OH). This can be attributed to the higher electron density at the secondary carbon, which facilitates nucleophilic attack on the boron center. However, the difference is small (6.0 kJ/mol), indicating that both hydroxyl groups can participate in the reaction under appropriate conditions.

The activation energy for bisglyceride borate formation (G–B–G) via intermolecular esterification of boric glycerides with glycerol ranges from 334.8 to 369.1 kJ/mol (Table 3). The relatively lower activation energies for triglyceride borate (336.6 kJ/mol) and 2-1-1'-2'-glyceride borate (334.8 kJ/mol) indicate that once the first boric acid molecule is attached, the remaining hydroxyl groups on the boric glyceride intermediate are activated for further esterification with additional glycerol molecules.

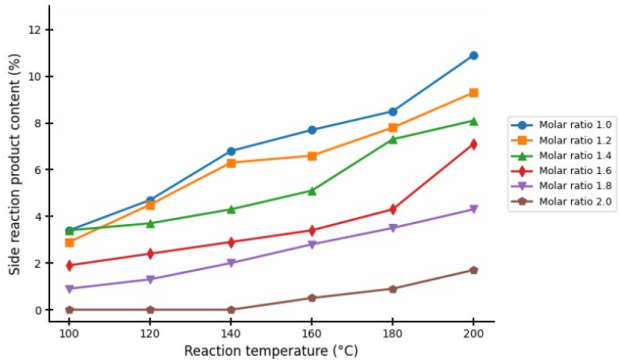


Figure 4. Change in the content of the by-products with reaction temperature and molar ratio.

Table 7. Energy change in the esterification reaction of boric acid glycerides (kJ/mol).

Product	Starting system	Transient state	Generation system	Activation energy
1-3-borate glyceride-2-ester	-836.9	-657.1	-830.7	179.8
2-1-borate glyceride-3-ester	-866.2	-693.9	-842.3	172.3
1-3-1'-3'-borate glyceride-2'-este	-1251.0	-1076.6	-1250.7	174.4
1-3-1'-3'-borate glyceride-2'-este	-1258.8	-1053.2	-1229.7	205.6
2-1-2'-1'- borate glyceride-3-este	-1307.5	-1130.8	-1245.5	176.7
2-1-2'-1'-borate glyceride-3'-este	-1316.3	-1101.7	-1293.3	214.6
2-1-1'-2'-borate glyceride-3-este	-1281.7	-1093.5	-1275.3	188.2
2-1-1'-2'-borate glyceride-3'-este	-1231.1	-1049.9	-1221.0	181.2
B-G-B-G-$OCOCH_3$	-2122.9	-1951.4	-2058.8	171.5

This stepwise activation mechanism is critical for achieving selective protection of two hydroxyl groups.

3.3. Scientific Interpretation of Monte Carlo Simulation Results

The Monte Carlo simulations (Table 5, Figure 2) provide quantitative predictions of product distribution under varying reaction conditions. At a glycerol-to-boric acid molar ratio of 2.0, the simulation predicts 100% protective glyceride content with 0% side products. This prediction is scientifically sound because at this stoichiometry, each boric acid molecule can react with two glycerol molecules, forming the desired G–B–G structure where two hydroxyl groups on each glycerol are protected by the borate ester, leaving one hydroxyl group free for subsequent esterification with stearic acid.

The temperature dependence (Table 6, Figures 3 and 4) reveals that lower temperatures (100–120 °C) favor selective protection, while higher temperatures (>160 °C) promote side reactions. This is consistent with the Arrhenius equation, where higher temperatures increase the rate of all reactions, including undesirable side reactions such as triester formation (complete protection of all three hydroxyl groups). The simulation results indicate that at 200 °C, even with the optimal molar ratio of 2.0, side product content increases to 1.7%, confirming that temperature control is essential for selectivity.

Comparison with literature: The use of Monte Carlo methods for predicting reaction outcomes in organic synthesis is well-established [10]. However, the application of this method to boric acid–glycerol esterification is novel. Traditional approaches rely on trial-and-error experimentation, which is time-consuming and resource-intensive. The present study demonstrates that computational screening can significantly reduce experimental effort, aligning with the principles of green chemistry and sustainable process development.

3.4. Scientific Interpretation of Bisglyceride Borate Synthesis Results

3.4.1. Effect of molar ratio

Experimental results (Figure 5) show that conversion increases with the glycerol-to-boric acid molar ratio, reaching 95.2% at 2:1. Above this ratio, unreacted glycerol accumulates, which would reduce the purity of the final product by forming di- and triglycerides during the subsequent esterification step. This experimental optimum (2:1) is in excellent agreement with the Monte Carlo simulation prediction (2:1), validating the computational approach.

3.4.2. Effect of reaction temperature

The conversion reaches 95.3% at 200 °C and remains constant at higher temperatures (Figure 6). However, product discoloration occurs at >200 °C, indicating thermal degradation of glycerol or boric acid. This observation is consistent with the known thermal instability of glycerol at elevated temperatures (>200 °C), where dehydration and polymerization can occur [11]. The use of toluene as an azeotropic dehydrating agent allows the reaction to proceed at a lower temperature (115 °C), while maintaining high conversion (96.0%), avoiding thermal degradation.

3.4.3. Effect of Azeotropic Dehydrating Agent

Toluene (0.5 L/mol boric acid) reduces the reaction temperature from 200 °C to 115 °C and shortens the reaction time from 90 min to 70 min, while increasing conversion from 95.3% to 96.0% (Figure 7). The azeotropic removal of water shifts the equilibrium toward product formation according to Le Chatelier's principle. This is a well-established strategy in esterification reactions [12,13].

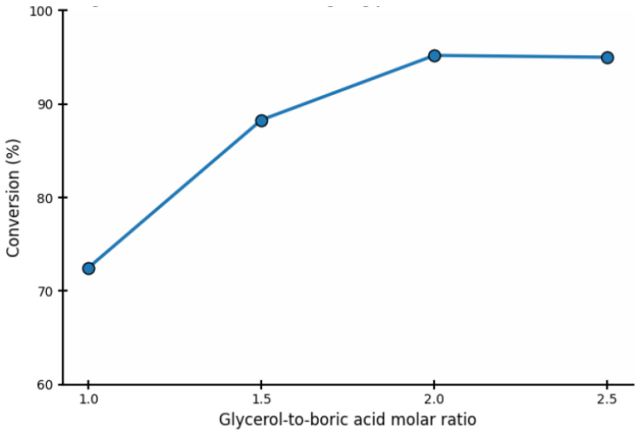


Figure 5. Conversion rate according to glycerol-to-boric acid molar ratio.

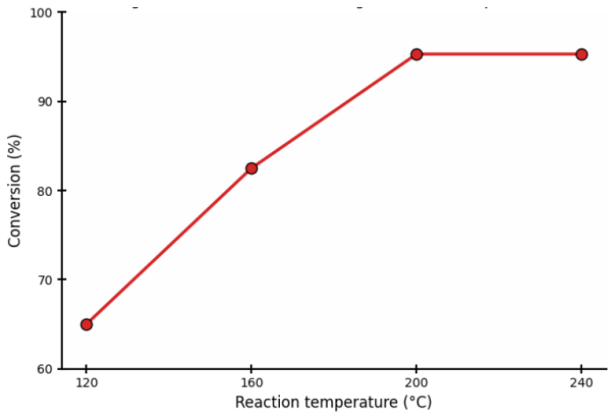


Figure 6. Conversion rate according to reaction temperature.

3.4.4. FT-IR characterization of bisglyceride borate

The FT-IR spectrum (Figure 8) confirms the formation of bisglyceride borate through characteristic bands: ν(O–H) at 3310 cm^{-1} (hydroxyl groups of glycerol), ν(C–O, alcohol) at 1111 cm^{-1}, ν(O–CH_2) at 1428 cm^{-1}, ν(C–H) at 2943 cm^{-1}, δ(CH_2, plane bending) at 759 cm^{-1}, and ν(B–O, coordination bond) at 830 cm^{-1}. The presence of the B–O band at 830 cm^{-1} is definitive evidence for borate ester formation, as this band is absent in free glycerol and boric acid [14].

The O–H stretching band at 3310 cm^{-1} is broad, indicating hydrogen bonding among the remaining free hydroxyl groups. This is expected because each glycerol unit in bisglyceride borate retains one free hydroxyl group, which can participate in intermolecular hydrogen bonding. The C–O stretching band at 1111 cm^{-1} is strong and sharp, characteristic of primary alcohol C–O bonds in glycerol derivatives.

3.5. Scientific Interpretation of Bisglyceride Borate-Stearate Synthesis Results

3.5.1. Effect of temperature, time, and catalyst

The esterification of bisglyceride borate with stearic acid reaches 95.3% conversion at 180 °C (Figure 9), 95.5% at 2.5 h (Figure 10), and 95.7% at 3% catalyst (Figure 11). The optimal conditions (140 °C, 90 min, 3% p-toluenesulfonic acid, with

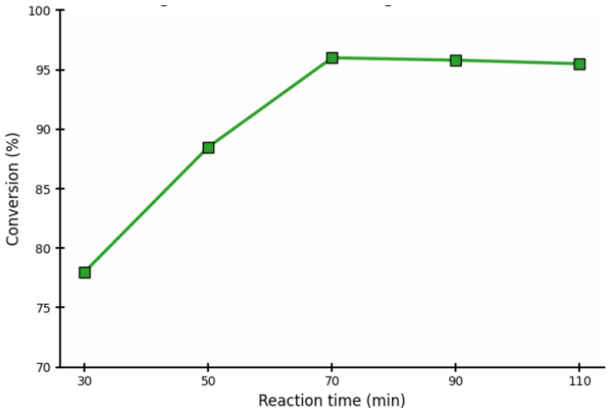


Figure 7. Conversion rate according to reaction time.

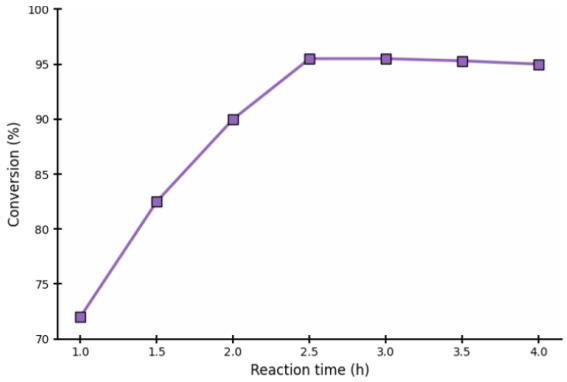


Figure 10. Conversion rate according to reaction time.

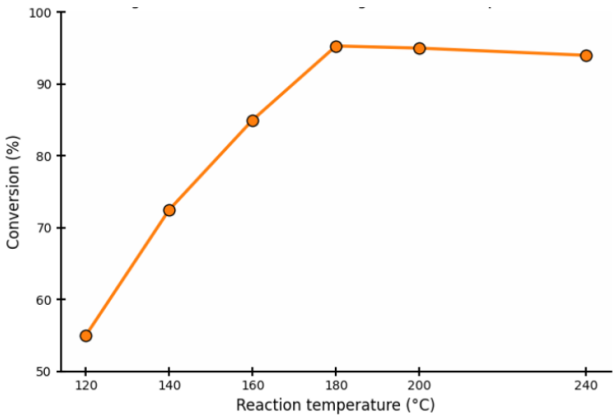


Figure 9. Conversion rate according to reaction temperature.

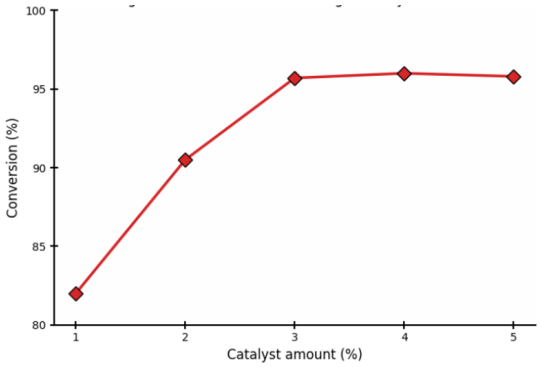


Figure 11. Conversion rate according to catalyst amount.

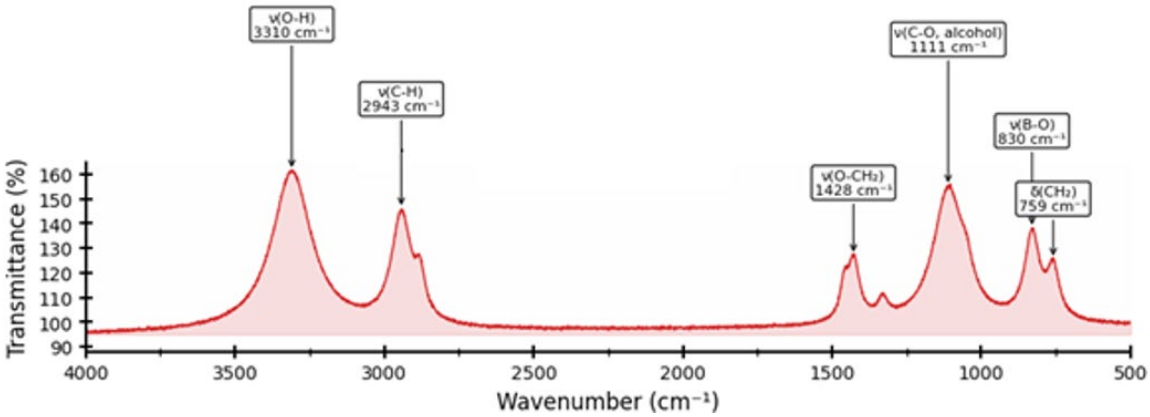


Figure 8. FT-IR spectrum of bisglyceride borate.

toluene) achieve 98.0% conversion (Table 8). The lower temperature requirement compared to the first step (140 °C vs. 115 °C with toluene) is due to the higher reactivity of the free hydroxyl group in bisglyceride borate and the acid catalysis by p-toluenesulfonic acid.

The similar activation energies for different boric glyceride structures with stearic acid (171.5–214.6 kJ/mol, Table 7) indicate that the steric and electronic effects of the borate protecting group do not significantly influence the esterification reactivity of the remaining free hydroxyl group. This is scientifically important because it means that the protecting group is "innocent"—it does not interfere with the desired reaction, which is a key requirement for an effective protecting group in organic synthesis [8].

3.5.2. FT-IR and melting point characterization

The FT-IR spectrum of bisglyceride borate-stearate (Figure 12) shows ν(C=O, ester) at 1738 cm^{-1}, confirming the formation of the ester linkage between the free hydroxyl group of bisglyceride borate and stearic acid. The presence of both ν(B–O) bands at 1177 and 1469 cm^{-1} indicates that the borate protecting group remains intact during the esterification. The O–H band at 3443 cm^{-1} is shifted to higher wavenumber compared to bisglyceride borate (3310 cm^{-1}), reflecting the change in hydrogen bonding environment after esterification. The melting point of 54–56 °C is consistent with the expected value for a glycerol derivative with one stearate ester and two borate-protected hydroxyl groups. This is lower than the melting point of glycerol monostearate (56 °C) because the borate groups disrupt the crystal packing of the stearate chains.

3.6. Scientific Interpretation of Glycerol Monostearate Synthesis and Validation

3.6.1. Hydrolysis and product isolation

Hydrolysis of bisglyceride borate-stearate with 2 mol/L HCl for 1 h cleaves the borate ester bonds, releasing boric acid (which is water-soluble and easily removed by washing) and yielding glycerol monostearate. The mild hydrolysis conditions (room temperature, dilute acid) are sufficient because borate esters are known to be labile under acidic aqueous conditions [8,9]. The product is recrystallized from ethanol at 55–60 °C, yielding white crystals with a melting point of 61–63 °C.

Table 8. Effect of toluene on reaction temperature and reaction time.

No	Toluene content (L/mol-boric acid)	Reaction time (min)	Reaction temperature (℃)	Rate of change (%)
1	0.000	150	180	95.7
2	0.150	120	170	90.6
3	0.175	100	163	93.2
4	0.200	110	155	92.7
5	0.225	100	150	95.5
6	0.250	90	140	98.0
7	0.275	90	140	97.6

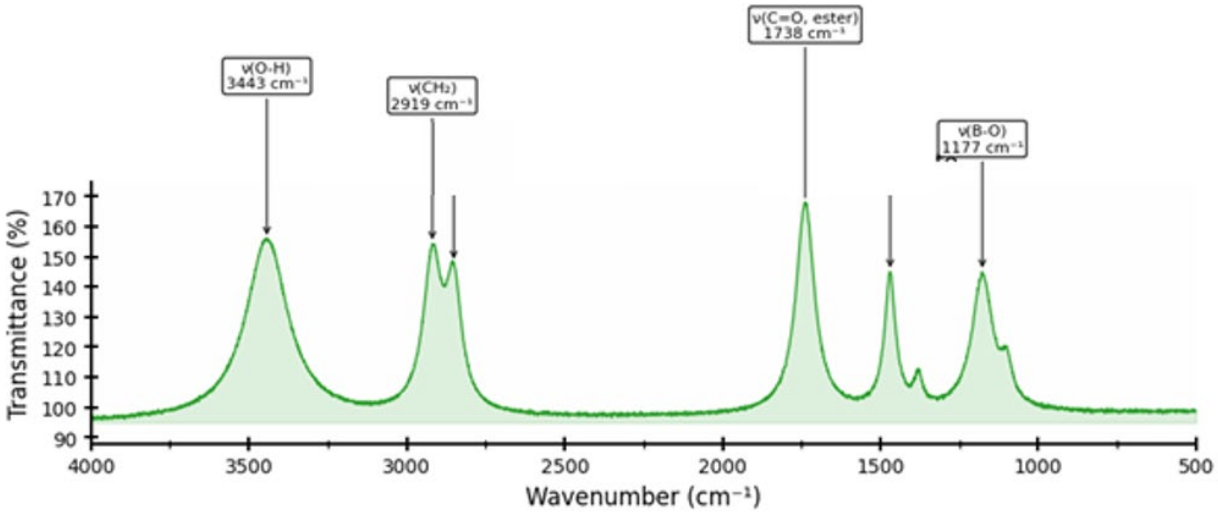


Figure 12. FT-IR spectrum of bisglyceride borate-stearate.

3.6.2. FT-IR characterization

The FT-IR spectrum of the final product (Figure 13) shows: ν(O–H) at 3335 cm^{-1} (broad, hydrogen-bonded hydroxyl groups), ν(C=O, ester) at 1733 cm^{-1} (strong, confirming the ester linkage), ν(CH_2) at 2919 and 2851 cm^{-1} (symmetric and asymmetric stretching of the stearate chain), ν(C–O) at 1106 cm^{-1} (C–O–C ester bond), and δ(CH_2) at 721 cm^{-1} (rocking vibration of the long alkyl chain). These bands are in excellent agreement with literature data for glycerol monostearate [14,15].

3.6.3. HPLC purity analysis

HPLC analysis (Figure 14) shows a major peak at 1.71 min with a purity of 95.15%. This retention time is consistent with glycerol monostearate on a reversed-phase C18 column with methanol as the mobile phase [15]. The absence of significant peaks at longer retention times (which would correspond to diglycerides and triglycerides) confirms that the boric acid protection method effectively prevents the formation of higher glycerides.

3.6.4. Physical properties

The physical properties of the synthesized product—melting point 61–63 °C, acid value 2.7, saponification value 160, HLB value 3.8—are consistent with standard glycerol monostearate specifications. The HLB value of 3.8 confirms the W/O emulsifier classification, which is in agreement with Whitenhurst [1] and other literature sources [4]. The low acid value (2.7) indicates minimal free fatty acid content, confirming the completeness of the esterification reaction and the effectiveness of the purification procedure.

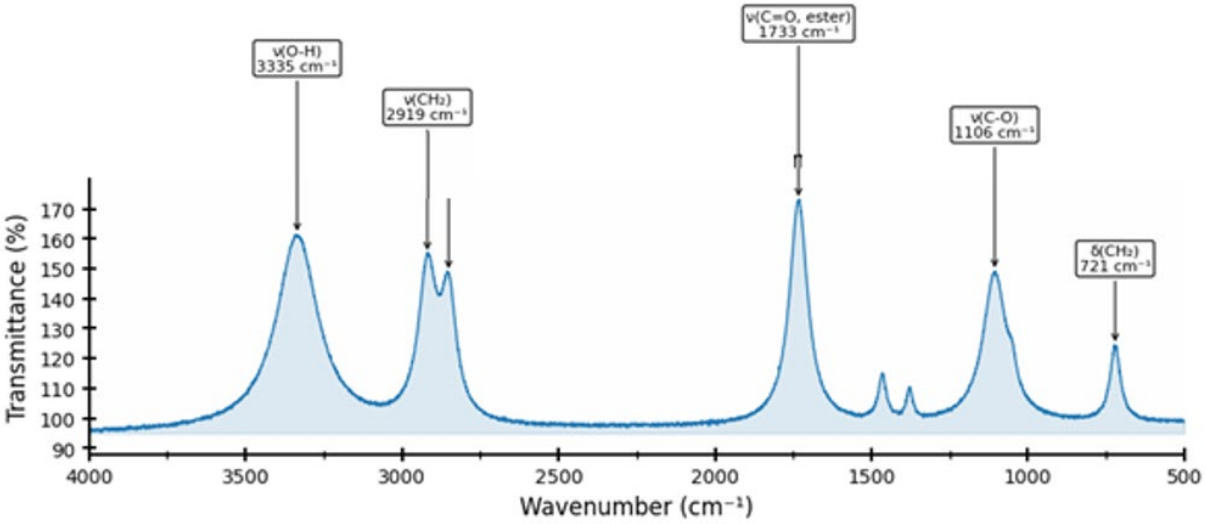


Figure 13. FT-IR spectrum of glycerol monostearate.

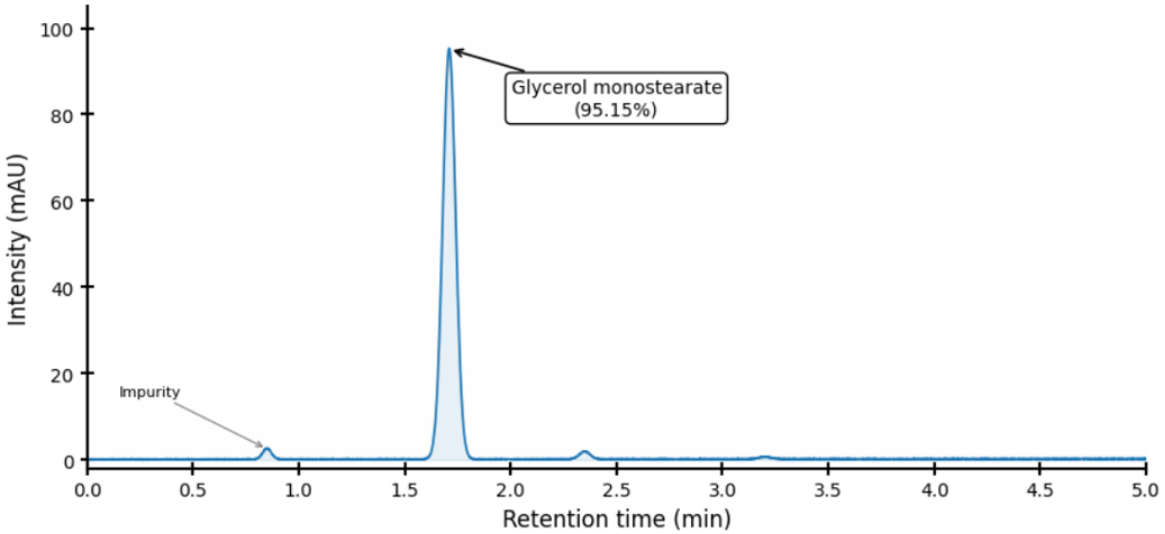


Figure 14. HPLC chromatogram of purified glycerol monostearate.

The boric acid protection method offers several advantages: (1) higher purity than direct esterification and enzymatic methods; (2) significantly lower equipment cost than molecular distillation; (3) simpler post-processing than all alternative methods; (4) shorter reaction time than enzymatic methods; (5) milder conditions than unprotected direct esterification. The only disadvantage is the use of boric acid, which requires careful handling and complete removal from the final product. However, the hydrolysis and washing steps effectively remove boric acid, as confirmed by the FT-IR absence of B–O bands in the final product (Figure 13).

4. Conclusions

This study developed a selective synthesis method for high-purity glycerol monostearate using boric acid ester protection, with the following key findings: (a) Theoretical Predictions: Quantum chemical calculations (AM1 method) revealed that intramolecular esterification of boric glycerides is more favorable than intermolecular esterification, and remaining hydroxyl groups of glycerol have reduced reactivity after ester formation. Monte Carlo simulations predicted optimal conditions for selective protection of two hydroxyl groups: glycerol-to-boric acid molar ratio 2:1, 115 °C (with toluene as dehydrating agent), 70 min. (b) Experimental Validation: Bisglyceride borate was synthesized under the predicted conditions with 96.0% conversion. Bisglyceride borate-stearate was synthesized at 140 °C (toluene), 90 min, 3% catalyst, with 98.0% conversion. Hydrolysis of the intermediate yielded glycerol monostearate with 95.15% purity (HPLC), matching standard properties via FT-IR, acid value, and saponification value analysis. (c) Advantages of the Method: Mild reaction conditions (115–140 °C) avoid reagent degradation. Simple post-processing (no molecular distillation) reduces costs. High product purity (>95%) meets industrial requirements for food and pharmaceutical applications. This method provides a scalable, cost-effective alternative for glycerol monostearate production, with significant industrial potential.

CRedit Author Statement

Author Contributions: Kyong Il Choe: Conceptualization, Investigation, Writing – original draft. Chol Min Ri: Investigation, Data curation, Validation. Jong Nam Kim: Visulaisation, Writing – review & editing. Rak Won Paek: Methodology, Formal analysis, Writing – review & editing. All authors have read and agreed to the published version of the manuscript.

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