Stereoisomerism in the Michael Addition Reaction of Dialkylcuprates to the 2-Cyclohexenones with C-4 Ester Substituents

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Stereoisomerism in the Michael addition of (Me₂C=CH)₂CuMgBr and (Me₂C=CH)₂CuLi to 3-alkyl/H-4-[(tert-butoxy carbonyl)alkyl]-2-cyclohexenone was studied. (Me₂C=CH)₂CuMgBr showed stereoselectivity in all cases (3-H, Me: anti; 3-n-Bu: syn). This stereoselectivity disappeared in the reaction of (Me₂C=CH)₂CuLi with 4-[(tert-butoxy carbonyl)methyl]-3-butyl-2-cyclohexenone. However, the stereoselectivity was recovered by elongating the 4-alkyl chain of 2-cyclohexenone to show the same selectivity as that of (Me₂C=CH)₂CuMgBr.

Key words: Michael addition

In many known cases of stereoselective Michael addition, some reports have described that interaction between the γ-oxygen of an α,β-unsaturated ketone and organometallic reagent was related to the stereoselectivity. We studied the stereoselectivity of Michael addition by using 3-alkyl/H-4-[(tert-butoxy carbonyl)alkyl]-2-cyclohexenones (1-4), which can be expected as precursors for the syntheses of steroids, and (Me₂C=CH)₂CuLi or (Me₂C=CH)₂CuMgBr to examine the effect on stereoselectivity of an ester-containing substituent at the 4-position. This report also describes the relationship between a substituent at the 3-position of 2-cyclohexenone and its stereoselectivity.

Results and Discussion

The four 2-cyclohexenone derivatives (1-4) were prepared from 3-ethoxy-2-cyclohexenone. After converting to 6-[(tert-butoxy carbonyl)methyl]-3-ethoxy-2-cyclohexenone, the keto ester was successively treated with sodium borohydride and acid to give 1. 2-Cyclohexenone 2 was obtained by the procedure described in the literature. Conversion to 6-[(tert-butoxy carbonyl)methyl]-3-ethoxy-2-cyclohexenone, and successive treatment with n-butyl magnesium bromide and acid gave 3. After 3-ethoxy-2-cyclohexenone had been converted to 6-[(tert-butoxy carbonyl)ethyl]-3-ethoxy-2-cyclohexenone by reaction with tert-butyl acrylate and potassium tert-butoxide in tert-butyl alcohol, the resulting keto ester was successively reacted with n-butyl magnesium bromide and acid to give 4.

Lithium cuprate or magnesium cuprate (1.5 eq.) was used in experiments on Michael addition reactions. Both Michael additions of (Me₂C=CH)₂CuLi and (Me₂C=CH)₂CuMgBr to 1 gave anti selectivity (Table, entries a and b). Anti-5 and syn-5 were determined by the coupling constants between 2-H (axial-H and equatorial-H) and 3-H (anti-5: Jaxialaxial=12.7 Hz, Jequatorialaxial=4.4 Hz; syn-5: Jaxialaxial=3.5 Hz, Jequatorialaxial=5.4 Hz). It has been reported that the Michael addition of (Me₂C=CH)₂CuMgBr to 2 gave anti-6 as a single isomer (Table, entry c). In the case of (Me₂C=CH)₂CuLi, anti-6 was also produced as a single isomer (Table, entry d). The same stereoselectivity between lithium cuprate and magnesium cuprate was observed in the Michael addition to 1 and 2. The absence of a substituent or the presence of a small substituent at the 3-position of 2-cyclohexenone is considered to favor the more stable anti product.

The Michael addition to 3, which has an n-butyl group at the 3 position and a (tert-butoxy carbonyl) methyl group at the 4 position, gave a mixture of anti and syn forms. To separate and determine the two isomers, the mixture of anti/syn-7 was converted to 3,5-dinitrobenzoate, anti-7" and syn-7". After the ketone group of the mixture of anti/syn-7 had been protected as dimethyl acetate by using dimethoxy orthoformaldehyde and p-toluenesulfonic acid in methanol, the resulting ester was reduced to an alcohol by lithium aluminum hydride. Separation of the anti and syn isomers was successful by converting to the 3,5-dinitrobenzoyl ester with 3,5-dinitrobenzoyl chloride in pyridine. Finally, hydrolysis of each of the acetals by hydrochloric acid in ethanol gave anti-7" and syn-7". NOE was observed between methyl groups on the Me₂C=CH group and two protons on the 2 position of anti-7". In the case of syn-7", the existence of NOE between methyl groups on the Me₂C=CH group and only the equatorial proton on the 2 position was found (Fig.). From these results, it became clear that Michael addition of magnesium cuprate preferentially gave the syn form (Table, entry e), while lithium cuprate showed no such selectivity (Table, entry g). The higher-order cyanocuprates showed the same selectivity (Table, entries f and h). The stereoselectivity of the lithium cuprate reaction could be recovered by adding HMPA to give syn selectivity (Table, entry j). The presence of HMPA in the magnesium cuprate reaction mixture did not change the selectivity (Table, entry i). These results seem to suggest chelation of the lithium atom to oxygen of the ester at the 4 position of 2-cyclohexenone. This chelation might enable nucleophiles to attack both sides of the C-3 carbon to produce anti-7 and syn-7 in a 1/1 ratio. Without this chelation, syn-7 was predominately obtained. The ratio

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of anti/syn when using lithium cuprate was influenced by the chain length of the 4-substituent of 2-cyclohexenone. Both Michael additions of lithium cuprate and magnesium cuprate to 4 having a n-butyl group at the 3-position and a 2-(tert-butoxycarbonyl)methyl group at the 4-position showed syn selectivity (Table, entries k and l). The fact that the major product of 8 had NOE between 2-equatorial H and the methyl groups on the Me₂C=CH group, but not between the 2-axial H and methyl groups on the Me₂C=CH group, supports this assignment. Even if there was chelation of lithium to oxygen of the ester at the 4 position of 2-cyclohexenone, elongation of the chain length of the 4-substituent inhibited the production of the anti form.

This report clarifies the stereoselectivity of Michael addition of organometallic nucleophiles to 3-alkyl/H-4-[(tert-butoxycarbonyl)alkyl]-2-cyclohexenone. The organomagnesium cuprate showed stereoselectivity in all cases. When the difference in stability between the anti and syn isomer was small, the organolithium cuprate showed no stereoselectivity, probably due to interaction between the lithium and oxygen of the ester function on the side chain at the 4 position of 2-cyclohexenone. Even in that case, stereoselectivity could be recovered by elongating the 4-alkyl chain of 2-cyclohexenone.

**Experimental**

All melting point (mp) data are uncorrected. NMR data were measured by JNM-EX400 and JEOL α500 spectrometers. EIMS and FABMS spectra were measured with Hitachi M-80B and JEOL HX-110 spectrometers, respectively. The silica gel used was Wakogel C-300 (Wako, 200-300 mesh), and preparative TLC was conducted with Merck silica gel 60F₂₅₄ (0.5 mm thickness, 20 x 20).

4-[(tert-Butoxycarbonyl)methyl]-2-cyclohexenone (1). To a solution of 6-[(tert-butoxycarbonyl)methyl]-3-ethoxy-2-cyclohexenone (5 g, 19.6 mmol) in ethanol (25 ml) was added sodium borohydride (0.37 g, 9.82 mmol). The reaction mixture was stirred at room temperature for 16 h before addition of a 2 N aqueous HCl solution (20 ml). After the resulting mixture was stirred at room temperature for 20 min, solid NaHCO₃ was added. The mixture was filtered, and the resulting filtrate was concentrated. The residue was dissolved in
ether and H₂O. The organic solution was separated, washed with brine, and dried (Na₂SO₄). Concentration followed by silica gel column chromatography (10% ethyl acetate/hexane) gave 1 (1.96 g, 9.32 mmol, 48%) as a colorless oil. 400 MHz ¹H-NMR δ(CDC1₃): 1.47 (9H, s, C(CH₃)₃), 1.70–1.80 (1H, m, 5-H), 2.12–2.19 (1H, m, 5-H), 2.33–2.54 (4H, m, CH₂CO₂Bu, 6-H), 2.91 (1H, m, 4-H), 6.00 (1H, dd, J = 10.0, 2.4 Hz, 3-H), 6.86 (1H, m, 2-H). EIMS m/z (70 eV): 211 (M⁺ + 1, 1), 203 (5), 195 (14), 185 (7), 171 (5), 155 (100), 137 (7), 109 (4). Anal. Found: C, 68.59; H, 8.86. Calcd. for C₁₂H₁₈O₂: C, 68.55, H, 8.63.

4-[(tert-Butyoxycarbonyl)methyl]-3-buty 1-2-cyclohexene (3). To a solution of n-butylnimogen bromide (23 mmol) in ether (20 mL) was added a solution of 6-[(tert-butyloxycarbonyl)methyl]-3-ethoxy-cyclohexene (4) (g, 16 mmol) in THF (20 mL) at −5°C. After the reaction mixture was stirred at −5°C for 1.5 h, a 2 N aqueous HCl solution (40 mL) was added. The resulting solution was stirred at room temperature for 20 min, and then solid NaCl (8 g) and ether were added. The organic solution was separated, washed with a saturated aqueous NaHCO₃ solution and brine, and dried (Na₂SO₄). Concentration followed by silica gel column chromatography (8% ethyl acetate/hexane) gave 4 (0.34 g, 1.21 mmol, 65%) as a colorless oil. 400 MHz ¹H-NMR δ(CDC1₃): 0.93 (3H, t, J = 7.3 Hz, (CH₃)₂CH), 1.31–1.52 (6H, m, (CH₂)₂CH₂), 1.46 (9H, s, C(CH₃)₃), 1.67–1.74 (1H, m, 5-H), 1.87–1.93 (2H, m, CH₂CH₂OBU), 2.01–2.07 (1H, m, 5-H), 2.23–2.38 (4H, m, CH₂CH₂CO₂Bu, 6-H), 2.40–2.50 (1H, m, 4-H), 5.84 (1H, s, 2-H). FABMS m/z: 303 (M + Na⁺), 44, 225 (100). HRMS (FAB) m/z (M + Na⁺): calcd. for C₁₂H₁₈O₂Na, 303.1937; found, 303.1935.

General procedure for Michael addition when using magnesium cuprate. a) A solution of (2-methyl-1-propenyl)magnesium bromide (1.5 eq.) in THF was added to a suspension of CuBr·Me₂S (0.2 eq.) in THF at −78°C. After 20 min at −78°C, a solution of the 2-cyclohexenone derivative (1 eq.) and trimethylsilyl chloride (6.5 eq.) in THF was added. The reaction mixture was stirred at −78°C for 1.5 h before additions of a 2 N aqueous HCl solution and ethyl acetate. The organic solution was separated, washed with a saturated aqueous NaHCO₃ solution and brine, and dried (Na₂SO₄). Concentration followed by silica gel column chromatography (3% ethyl acetate/hexane) gave the product. b) A solution of thiophene (1.5 eq.) in THF was added n-butyllithium (1.5 eq.) in hexane at −50°C. The mixture was stirred at −20°C for 1 h and then CuCN (1.5 eq.) was added. After 20 min at room temperature, the mixture was cooled to −78°C. To the mixture was sequentially added a solution of (2-methyl-1-propenyl)magnesium bromide (1.5 eq.) in THF, BF₄·OEt₂ (1.5 eq.), HMPA (omitted or 5 eq.), and the 2-cyclohexenone derivative (1.0 eq.) in THF. After 1.5 h at −78°C, the reaction was quenched by additions of a 2 N aqueous HCl solution and ethyl acetate. The organic solution was separated, washed with a saturated aqueous NaHCO₃ solution and brine, and dried (Na₂SO₄). Concentration followed by silica gel column chromatography (3% ethyl acetate/hexane) gave the product.

General procedure for Michael addition when using lithium cuprate. a) To a solution of 2-methylpropenyllithium (1.5 eq.) in THF was added CuBr·Me₂S (0.5 eq.). After the mixture was stirred at −78°C for 30 min, a solution of the 2-cyclohexenone derivative (1 eq.) and trimethylsilyl chloride (6.5 eq.) in THF was added. The reaction mixture was stirred at −78°C for 1.5 h and quenched by additions of a 2 N aqueous HCl solution and ethyl acetate. The organic solution was separated, washed with a saturated aqueous NaHCO₃ solution and brine, and dried (Na₂SO₄). Concentration followed by silica gel column chromatography (3% ethyl acetate/hexane) gave the product. b) To a suspension of CuCN (1.5 eq.) in THF were added methylithium (3 eq.) in ether and tributyl 2-methyl-1-propenyl stannane (1.5 eq.) in ether at 0°C. After stirring at room temperature
4. [(tert-Butyoxycarbonyl)methyl]-3-(2-methyl-1-propenyl)cyclohexane (T). 400 MHz $^1$H-NMR $\delta_H$(CDCl$_3$): 0.88 (2H, t, $J=6.8$ Hz), 0.89 (0H, t, $J=6.8$ Hz), 1.15–1.35 (6H, m), 1.35–1.60 (2H, m), 1.47 (9H), 1.69–1.75 (4H, m), 1.93–2.01 (0.3H, m), 2.01–2.10 (0.7H, m), 2.10–2.19 (1H, m), 2.25–2.40 (3H, m), 2.50–2.61 (2H, m), 4.83 (0.3H, s, CH$_2$=CH(C$_2$H$_5$)), 4.96 (0.7H, s, CH=CH(C$_2$H$_5$)). HRMS (FAB) m/z: 345 (M+Na$^+$, 36), 267 (100), 249 (57), 211 (91), 209 (53), 165 (42).

3-Butyl-3-(2-methyl-1-propenyl)-4-[2-(3,5-dinitrobenzoyloxy)ethyl]cyclohexane (7'). A solution of a 3/7 mixture of anti/syn-7 (0.2 g, 0.62 mmol), trimethyl orthoformate (0.14 ml, 1.24 mmol), and $p$-toluenesulfinic acid (0.01 g) in methanol (15 ml) was refluxed for 2 h. After addition of triethylamine (0.1 ml), the solution was concentrated. The residue was applied to silica gel column chromatography (5% ethyl acetate/hexane) to give a 3/7 mixture of anti/syn-1-[(tert-butoxycarbonyl)methyl]-2-butyl-4,4-dimethoxy-2-(2-methyl-1-propenyl) cyclohexane (0.17 g, 0.46 mmol, 74%) as a colorless oil. 400 MHz $^1$H-NMR $\delta_H$(CDCl$_3$): 0.88–0.91 (3H, m), 1.15–1.39 (4H, m), 1.16–1.64 (7H, m), 1.44 (9H, s), 1.69–1.75 (6H, m), 1.80–1.86 (2H, m), 1.96–2.04 (1H, m), 2.33–2.40 (1H, m), 3.08 (0.9H, s), 3.12 (0.9H, s), 3.15 (4.2H, s), 5.09 (1H, s).

To a suspension of lithium aluminum hydride (28 mg, 0.738 mmol) in ether (3 ml) was added the 3/7 mixture of anti/syn-1-[(tert-butoxycarbonyl)methyl]-2-butyl-4,4-dimethoxy-2-(2-methyl-1-propenyl)cyclohexane (0.17 g, 0.46 mmol) in ether (2 ml) at 0°C. The reaction mixture was stirred at room temperature for 1.5 h. To the reaction mixture were added a saturated aqueous MgSO$_4$ solution (0.5 ml) and K$_2$CO$_3$ (0.5 g) at 0°C. After stirring at room temperature for 10 min, the mixture was filtered. The filtrate was dried (Na$_2$SO$_4$) and concentrated. The residue was applied to silica gel column chromatography (25% ethyl acetate/hexane) to give a 3/7 mixture of anti/syn-2-butyl-1-(2-hydroxyethyl)-4,4-dimethoxy-2-(2-methyl-1-propenyl)cyclohexane (0.13 g, 0.44 mmol, 94%) as a colorless oil. 400 MHz $^1$H-NMR $\delta_H$(CDCl$_3$): 0.87–0.92 (3H, m), 1.18–1.38 (6H, m), 1.54 (1H, d, $J=13.7$ Hz), 1.52–1.79 (6H, m), 1.70–1.73 (6H, m), 1.80–1.94 (2H, m), 3.07 (0.9H, s), 3.12 (0.9H, s), 3.15 (4.2H, s), 3.52–3.65 (1H, m), 3.68–3.75 (1H, m), 5.10 (0.3H, s), 5.16 (0.7H, s).

A reaction mixture of 3,5-dinitrobenzoyl chloride (0.15 mg, 0.65 mmol) and a 3/7 mixture of anti/syn-2-butyl-1-(2-hydroxyethyl)-4,4-dimethoxy-2-(2-methyl-1-propenyl)cyclohexane (0.13 g, 0.44 mmol) in pyridine (3 ml) was stirred at room temperature for 16 h. After dilution with ether (30 ml), the organic solution was washed with water, a saturated aqueous NaHCO$_3$ solution, and brine, and then dried (Na$_2$SO$_4$). Concentration followed by silica gel column chromatography (1% ethyl acetate/benzene) gave anti-2-butyl-4,4-dimethoxy-2-(2-methyl-1-propenyl)-1-[2-(3,5-dinitrobenzoyloxy)ethyl]cyclohexane (33 mg, 0.067 mmol, 15%) and syn-2-butyl-4,4-dimethoxy-2-(2-methyl-1-propenyl)-1-[2-(3,5-dinitrobenzoyloxy)ethyl]cyclohexane (77 mg, 0.16 mmol, 36%) as colorless oils, respectively. Anti isomer: 400 MHz $^1$H-NMR $\delta_H$(CDCl$_3$): 0.86 (3H, t, $J=7.3$ Hz), 1.20–1.35 (5H, m), 1.42–1.63 (6H, m), 1.74 (6H, s), 1.70–1.92 (3H, m), 2.00–2.10 (1H, m), 3.09 (3H, s), 3.16 (3H, s), 4.42–4.52 (1H, m), 4.53–4.61 (1H, m), 5.16 (1H, s), 9.15–9.17 (2H, m), 9.22–9.25 (1H, m). Syn isomer: 400 MHz $^1$H-NMR $\delta_H$(CDCl$_3$): 0.89 (3H, t, $J=6.8$ Hz), 1.10–1.55 (7H, m), 1.56–1.97 (6H, m), 1.71–1.72 (6H, m), 1.96–1.98 (1H, m), 1.99–2.10 (1H, m), 3.14 (3H, s), 3.17 (3H, s), 4.38–4.42 (1H, m), 4.43–4.52 (1H, m), 5.12 (1H, s), 9.15–9.17 (2H, m), 9.22–9.25 (1H, m).

Michael Addition Reaction to 2-cyclohexenones with C-4 Ester Substituents. 767.
Each of the benzoates was hydrolyzed to $\text{H}^+$ by using a 1 N aqueous HCl solution in ethanol in a quantitative yield. Purification by silica gel TLC (2% ethyl acetate/benzene) gave anti-$\text{H}^+$ and syn-$\text{H}^+$. Anti-$\text{H}^+$: mp 105–107°C; 500 MHz $^1\text{H}$-NMR $\delta_{\text{H}}$ (CDCl$_3$): 0.87 (3H, t, $J$ = 7.2 Hz, (CH$_3$)$_2$CH), 1.19–1.32 (4H, m, (CH$_2$)$_2$CH), 1.44–1.50 (1H, m, (CH$_2$)$_2$CH), 1.56–1.63 (1H, m, (CH$_2$)$_2$CH), 1.72 (3H, d, $J$ = 1.4 Hz, CH$_3$), 1.74 (3H, d, $J$ = 1.4 Hz, CH$_3$), 1.75–1.83 (2H, m, O=CO-CH=CH$_2$), 1.87 (1H, m, 4-H), 2.08 (1H, m, 5-H), 2.23–2.31 (2H, m, O=CO-CH=CH$_2$, 6-H), 2.35–2.42 (1H, m, 6-H), 2.37 (1H, d, $J$ = 14.2 Hz, 2-axial H), 2.62 (1H, d, $J$ = 14.2 Hz, 2-equatorial H), 4.49–4.59 (2H, m, O=COCH$_3$), 4.91 (1H, m, CH=CH$_2$), 9.15–9.16 (2H, m, ArH), 9.23 (1H, dd, $J$ = 2.1, 2.1 Hz, ArH). 125 MHz $^{13}$C-NMR $\delta_{\text{C}}$ (CDCl$_3$): 14.01 ((CH$_3$)$_2$CH), 19.56 (C=CH(CH$_3$)$_2$), 23.26 ((CH$_2$)$_2$CH), 25.91 ((CH$_2$)$_2$CH), 25.99 (5-C), 27.98 (O=COCH$_3$), 28.78 (CH=CH$_2$), 38.41 ((CH$_2$)$_2$CH), 38.59 (6-C), 40.07 (4-C), 46.57 (3-C), 49.35 (2-C), 65.95 (O=COCH$_3$), 122.42, 126.71 (CH=CH(CH$_3$)$_2$), 129.33, 133.95, 134.14 (CH=CH(CH$_3$)$_2$), 148.81, 162.53 (O=CO), 210.83 (1-C). FABMS m/z: 469 (M+Na$^+$, 17), 176 (66), 136 (62), 73 (100). HRMS (FAB) m/z: 470 (M+Na$^+$, 1): 125 MHz $^1\text{H}$-NMR $\delta_{\text{H}}$ (CDCl$_3$): 0.89 (3H, t, $J$ = 7.0 Hz, (CH$_2$)$_2$CH), 1.20–1.32 (4H, m, (CH$_2$)$_2$CH), 1.35–1.41 (1H, m, (CH$_2$)$_2$CH), 1.42–1.44 (1H, m, (CH$_2$)$_2$CH), 1.72–1.77 (1H, m, O=COCH$_3$CH$_2$), 1.74 (6H, s, C=CH(CH$_3$)$_2$), 1.78–1.82 (1H, m, 5-H), 2.11–2.16 (2H, m, 4-H, 5-H), 2.16–2.22 (1H, m, O=COCH$_3$CH$_2$), 2.32–2.37 (2H, m, 6-H), 2.34 (1H, d, $J$ = 13.9 Hz, 2-axial H), 2.62 (1H, d, $J$ = 13.9 Hz, 2-equatorial H), 4.47–4.52 (1H, m, O=COOCH$_3$), 4.54–4.59 (1H, m, O=COCH$_3$), 5.02 (1H, m, CH=CH(CH$_3$)$_2$), 9.16 (2H, s, ArH), 9.23 (1H, t, $J$ = 2.1 Hz, ArH). 125 MHz $^{13}$C-NMR $\delta_{\text{C}}$ (CDCl$_3$): 14.01 ((CH$_3$)$_2$CH), 19.36 (C=CH$_2$), 23.48 ((CH$_2$)$_2$CH), 25.89 ((CH$_2$)$_2$CH), 26.56 (5-C), 27.66 (O=COCH$_3$CH$_2$), 28.56 (CH=CH(CH$_3$)$_2$), 34.70 (CH$_2$), 38.83 (6-C), 39.67 (4-C), 46.38 (3-C), 49.32 (2-C), 66.03 (O=COCH$_3$), 122.42, 129.32, 129.66 (CH=C(CH$_3$)$_2$), 133.58 (CH=C(CH$_3$)$_2$), 133.96, 148.80, 162.51 (O=CO), 210.68 (1-C). FABMS m/z: 469 (M+Na$^+$, 65), 176 (100), 154 (67), 136 (66). HRMS (FAB) m/z: (M+Na$^+$): calcld. for C$_{23}$H$_{36}$O$_2$N$_2$Na, 469.1951; found, 469.1943.

4-[2-(tert-Butyloxycarbonyl)ethyl]-3-butil-3-(2-methyl-1-propenyl)cyclohexanone (8). 400 MHz $^1\text{H}$-NMR $\delta_{\text{H}}$ (CDCl$_3$): 0.88 (3H, t, $J$ = 7.3 Hz), 1.23–1.28 (5H, m), 1.32–1.40 (1H, m), 1.46 (9H, s), 1.50–1.58 (2H, m), 1.70 (3H, d, $J$ = 1.0 Hz), 1.71 (3H, d, $J$ = 1.0 Hz), 1.88–1.96 (1H, m), 1.97–2.02 (2H, m), 2.16–2.27 (2H, m), 2.27–2.39 (2.2H, m), 2.29 (0.8H, d, $J$ = 13.7 Hz, 2-axial H), 2.54 (0.8H, d, $J$ = 13.7 Hz, 2-equatorial H), 2.60 (0.2H, d, $J$ = 13.7 Hz, 2-equatorial H), 4.90 (0.8H, s, CH=CH(CCH$_3$)$_2$), 4.96 (0.2H, s, CH=CH(CCH$_3$)$_2$). FABMS m/z: 359 (M+Na$^+$, 100), 263 (58), 225 (79), 223 (45), 165 (32). HRMS (FAB) m/z: (M+Na$^+$): calcld. for C$_{23}$H$_{36}$O$_2$N$_2$Na, 359.2562; found, 359.2566.

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