A New Synthetic Route to the Synthesis of Nordasycarpidone Derivatives

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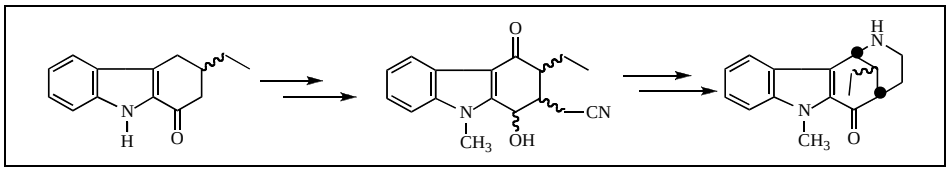

A new synthetic route for the synthesis of the nordasycarpidone derivative **11** which has hexahydro-1,5-methanoazocino[4,3-*b*]indol skeleton, is described. Construction of the tetracyclic structure was achieved by catalytic reduction and cyclization reaction of the nitrile derivative. Also many new tetrahydrocarbazole derivatives (**4**, **5**, **6**, **7**, **8**, **9**) and a dasycarpidol derivative (**10**) were synthesized.

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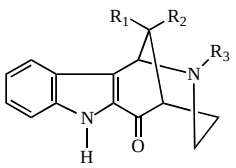
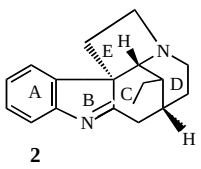
Several routes to tetracyclic dasycarpidone derivatives (**1a, 1b, 1c, 1d**) of the strychnos-type alkaloids have been reported in the literature. Most of routs start with the aromatic A-ring and the heterocyclic D-ring and build the tetracyclic skeleton by closing the B and C in subsequent steps [1-8]. There are also a few attempts for the construction of D-ring from tetrahydrocarbazole derivatives *via* acid catalyst ring closure or intramolecular Aldol reaction [9-12]. In this paper we describe a synthetic route utilizing tetrahydrocarbazole which bears a nitrile side chain at the position 2 (carbazole numbering) as a key intermediate. This carbazole derivative allows the closure of the D-ring in the last synthetic step *via* catalytic hydrogenation, yielding a tetracyclic dasycarpidone alkaloid. The scope of this route is also valuable for the construction of the pentacyclic strychnos alkaloid condyfoline (**2**) [13-15].





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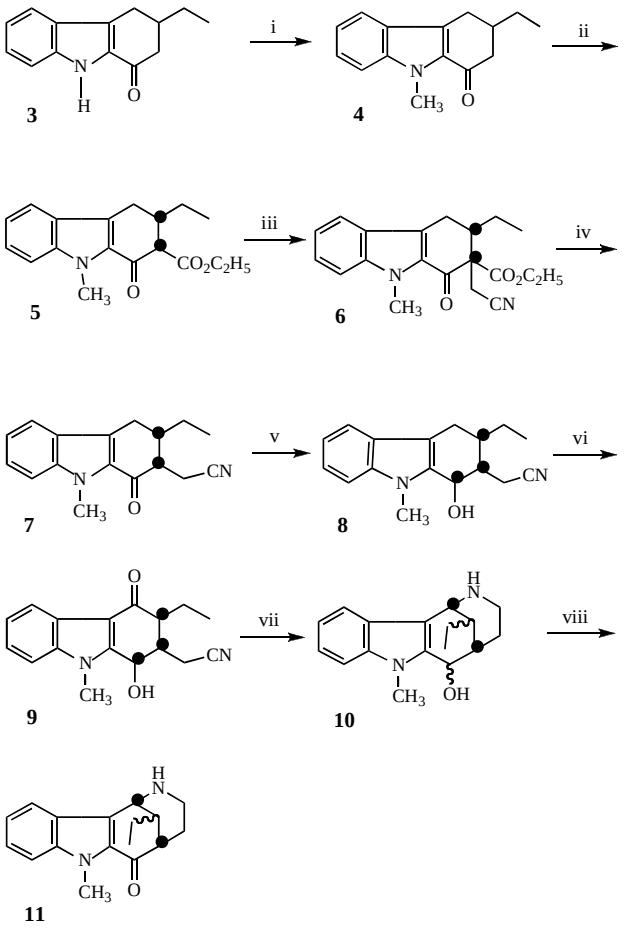
1a R_1: C_2H_5, R_2: H, R_3: CH_3 dasycarpidone
1b R_1: H, R_2: C_2H_5, R_3: CH_3 epidasycarpidone
1c R_1: C_2H_5, R_2: H, R_3: H nordasycarpidone
1d R_1: H, R_2: C_2H_5, R_3: H norepidasycarpidone

Herein, we have synthesized the nordasycarpidone derivative **11** in eight steps and 5 % overall yield (Scheme 1). For this target we selected 3-ethyl-1,2,3,4-tetra-hydrocarbazole-1-one (**3**) as the starting material which has been synthesized previously [16]. Indol nitrogen atom of **3** was protected by methylation with potassium hydroxide and methyl iodide in acetone which yielded **4** [17]. Later we activated α-position of carbonyl group of **4** using potassium hydride and diethyl carbonate which resulted in

Scheme 1



Reagents and conditions: i) KOH, CH_3I, acetone, 0 ºC, 2 h, 84%; ii) KH, $(C_2H_5O)_2CO$, 0 ºC, reflux, 1h, 66%; iii) Cs_2CO_3, ICH_2CN, tert-ButOH, reflux, 3h, 92%; iv) KOH, H_2O-$(CH_3)_2CHOH$, rt, 5h, 80%; v) $CeCl_3.7H_2O$, $NaBH_4$, 15 min. 0 ºC , 2h rt, 87%; vi) DDQ, THF(90%), N_2, 0 ºC, 3h, 66%; vii) C_2H_5OH, PtO_2, H_2, 5 days, 30%; viii) CH_2Cl_2, MnO_2, rt, 3h, 73%.

compound **5** [18]. Cyanomethylation of compound **5** utilizing cesium carbonate and iodoacetonitrile in tert-butyl alcohol gave the compound **6** [17,19]. Compound **7** was obtained by hydrolysis and decarboxylation of **6** with potassium hydroxide [19]. Reduction of the carbonyl group in compound **7** was carried out with sodium borohydride in methanol and yielded **8** [19]. Compound **8** was oxidized selectively at 4 position using 2,3-dichloro-5,6-dicyano-p-benzoquinone which yielded compound **9** [20]. Catalytic hydrogenation of the compound **9** using platinum(IV) oxide as a catalyst, yielded tetracyclic structure **10** [21]. Finally, the oxidation of **10** with active manganese (IV) oxide gave a (±)-nordasycarpidone derivative as an epimeric mixture **11** [22, 23].

EXPERIMENTAL

All melting points were measured in sealed tubes using an electrothermal digital melting point apparatus (Gallenkamp) and uncorrected. Infrared spectra were recorded on a Hitachi 270-30 infrared spectrometer. ^{1}H nmr spectra were obtained on a high resolution Fourier Transform Bruker WH-400 NMR spectrometer with tetramethylsilane as an internal standard. Mass spectra were determined a Micromass UK Platform II LC-MS spectrometer and a HP 5971 mass and combined 5980 gas chromatography system. Combustion analysis of compounds was obtained on a CHNS-932-LECO. Analytical and preparative thin layer chromatography (TLC) was carried out using silica gel 60 HF-254 (Merck). Column chromatography was carried out by using 70-230 mesh silica gel (0.063-0.2 mm, Merck) and aluminum oxide 90 active neutral (Merck).

3-Ethyl-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazole-1-one (4). To a solution of 2.50 g (11.72 mmoles) of **3** in 50 ml of acetone were added 1.97 g (35.11 mmoles) of potassium hydroxide and 4.16 g (29.31 mmoles) methyl iodide at 0 ºC. The reaction mixture was stirred for 2 hours at room temperature. The reaction mixture was acidified with 25 ml of 6 *N* hydrochloric acid solution and extracted with chloroform. The organic layer was dried with anhydrous magnesium sulfate, and the solvent was removed. The residue was purified by chromatography using silica gel and ethyl acetate-hexane (1:1). After the solvent was evaporated, the product was recrystallized from ether to afford 2.25 g (84%) of **4**, mp: 104-105 ºC; rf: 0.41 (ethyl acetate); ir (potassium bromide): ν 2959 (CH), 1659 (C=O, ketone) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.12 (3H, t, J= 7.18 Hz, CH_2CH_3), 1.52-1.64 (2H, m, CH_2CH_3), 2.25-2.38 (1H, m, HC_4H), 2.45-2.52 (1H, m, HC_4H), 2.58 (1H, dd, J= 16.2 and 3.9 Hz, C_2H), 2.77-2.84 (1H, m, C_3H), 3.20 (1H, dd, J= 16.5 and 11.7 Hz, C_2H), 4.03 (3H, s, NCH_3), 7.15-7.31 (2H, m, aromatic protons), 7.44 (1H, d, J= 8.2 Hz, aromatic proton), 7.86 (1H, d, J= 7.9 Hz, aromatic proton); ms: m/z 228(7.3) $[M+1]^+$, 227(7.3) $[M]^+$, 198(34.5) $[M-C_2H_5]^+$, 170(17.4) $[M-C_3H_5O]^+$, 156(28.4) $[M-C_4H_7O]^+$, 143(100) $[M-C_5H_8O]^+$,128(14.8) $[M-C_6H_{11}O]^+$; *Anal.* Calcd. for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.40; H, 7.55; N, 6.12.

Ethyl 3-ethyl-9-methyl-1-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (5). A solution of 2 g (8.8 mmoles) of **4** in 25 ml of diethyl carbonate was added dropwise to a mixture of 2.2 g (35% dispersion in mineral oil, 19.36 mmoles) of potassium hydride in 50 ml of diethyl carbonate at 0 ºC. The reaction mixture was refluxed for 1 hour and then poured into 100 ml of ice-water. The aqueous layer was extracted with ethyl acetate. The combined organic phase was dried with anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure and the resulting residue was chromatographed using silica gel and ethyl acetate-hexane (1:2). The solvent was removed and then the product was recrystallized from methanol to afford 1.75 g (66%) of **5**, mp: 164-165 ºC; rf: 0.62 (ethyl acetate); ir (potassium bromide): ν 2968 (CH), 1737 (C=O, ester), 1658 (C=O, ketone) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.12 (3H, t, J= 7.18 Hz, CH_2CH_3), 1.16 (3H, t, J= 7.12 Hz, OCH_2CH_3), 1.51-1.63 (2H, m, CH_2CH_3), 2.40-2.47 (1H, m, HC_4H), 2.52-2.59 (1H, m, HC_4H), 2.80-2.87 (1H, m, C_3H), 3.55 (1H, d, J= 9.8 Hz, C_2H), 4.05 (3H, s, NCH_3), 4.10 (2H, q, J= 7.13 Hz, OCH_2CH_3), 7.18-7.34 (2H, m, aromatic protons), 7.50 (1H, d, J= 8.1 Hz, aromatic proton), 7.94 (1H, d, J= 8.0 Hz, aromatic proton); ms: m/z 300(4.3) $[M+1]^+$, 299(18.5) $[M]^+$, 254(10.4) $[M-C_2H_5O]^+$, 226(47.5) $[M-C_3H_5O_2]^+$, 197(35.4) $[M-C_5H_{10}O_2]^+$, 169(22.7) $[M-C_6H_{10}O_3]^+$, 143(100) $[M-C_8H_{12}O_3]^+$. *Anal.* Calcd. for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.16; H, 7.09; N, 4.60.

Ethyl 2-(cyanomethyl)-3-ethyl-9-methyl-1-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-2-carboxylate (6). A mixture of 2.5 g (8.4 mmoles) of **5**, 3 g (9.2 mmoles) of cesium carbonate and 1.54 g (9.2 mmoles) of iodoacetonitrile in 50 ml of *tert*-butyl alcohol was refluxed for 3 hours under a nitrogen atmosphere. The reaction mixture poured into 50 ml of 5% hydrochloric acid solution and extracted with ethyl acetate. The solvent was evaporated under reduced pressure and the resulting residue was chromatographed using silica gel and ethyl acetate-hexane (1:1). The solvent was removed and then the product was recrystallized from methanol to afford 2.60 g (92%) of **6**, mp: 122-123 ºC; rf: 0.47 (ethyl acetate); ir (potassium bromide): ν 2967 (CH), 2248 (CN), 1731 (C=O, ester), 1651 (C=O, ketone) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.13 (3H, t, J= 7.14 Hz, CH_2CH_3), 1.15 (3H, t, J= 7.13 Hz, OCH_2CH_3), 1.32-1.44 (1H, m, $HCHCH_3$), 1.72-1.83 (1H, m, $HCHCH_3$), 1.88-1.96 (1H, m, C_3H), 2.57 (dd, 1H, J= 16.49 and 5.82 Hz, HC_4H), 2.69 (dd, 1H, J= 11.62 and 5.82 Hz, HC_4H), 2.82 (2H, s, CH_2CN), 4.10 (3H, s, NCH_3), 4.20 (2H, q, J= 7.13 Hz, OCH_2CH_3), 7.14-7.32 (2H, m, aromatic protons), 7.68 (1H, d, J= 7.9 Hz, aromatic proton), 8.02 (1H, d, J= 8.0 Hz, aromatic proton); ms: m/z 339(4.1) $[M+1]^+$, 338(16.5) $[M]^+$, 293(14) $[M-C_2H_5O]^+$, 265(41) $[M-C_3H_5O_2]^+$, 225(36) $[M-C_5H_7NO_2]^+$, 197(100) $[M-C_6H_7NO_3]^+$, 143(62) $[M-C_{10}H_{13}NO_3]^+$. *Anal.* Calcd. for $C_{20}H_{22}N_2O_3$: C, 70.98; H, 6.55; N, 8.28. Found: C, 70.87; H, 6.47; N, 8.36.

(3-Ethyl-9-methyl-1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)acetonitrile (7). A 0.5 *M* 100 ml solution of potassium hydroxide in water-isopropyl alcohol (1:5) was added to 2 g (5.9 mmoles) of **6** and the reaction mixture was stirred for 5 hours. Then the mixture was poured into 50 ml of cold water and extracted with ether. The organic layer was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel using ethyl acetate-hexane (1:1). After the solvent was evaporated, yielded 1.26 g (80%) of **7,** mp: 142-143 ºC, rf: 0.39 (ethyl acetate); ir (potassium bromide): ν 2937 (CH), 2246 (CN), 1642 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.11 (3H, t, J= 7.12 Hz, CH_2CH_3), 1.28-1.36 (1H, m, $HCHCH_3$), 1.48-1.60 (1H, m, $HCHCH_3$), 1.82-1.94 (1H, m, C_3H), 2.51 (1H, dd, J= 16.21 and 5.85 Hz, C_4H), 2.62 (1H, dd, J= 11.67 and 5.85

Hz, C_4H), 2.67-2.73 (1H, m, C_2H), 2.78-2.84 (2H, m, CH_2CN), 4.06 (3H, s, NCH_3), 7.11-7.28 (2H, m, aromatic protons), 7.47 (1H, d, J= 7.8 Hz, aromatic proton), 7.96 (1H, d, J= 8.1 Hz, aromatic proton); ms: m/z 267(12) $[M+1]^+$, 266(28) $[M]^+$, 240(14) $[M-CN]^+$, 226(100) $[M-C_2H_2N]^+$, 197(42) $[M-C_4H_7N]^+$. *Anal.* Calcd. for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.54; H, 6.83; N, 10.48.

(3-Ethyl-1-hydroxy-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)acetonitrile (8). To a solution of 2 g (7.5 mmoles) of **7** in 50 ml of methanol was added 3 g (8.3 mmoles) of cerium (III) chloride heptahydrate at 0 ºC and stirred for 15 minutes. Then 0.57 g (15 mmoles) of sodium borohydride was added and stirred for 2 hours at room temperature. The reaction mixture was diluted with 100 ml of 10% hydrochloric acid and extracted with ether. The organic layer was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. Then the residue was recrystallized from ether to afford 1.75 g (%87) of **8**, mp: 172-173 ºC; ir (potassium bromide): ν 3440 (OH), 2953 (CH), 2249 (CN) cm^{-1}; ^1H nmr (deuterio dimethylsulfoxide): δ 1.15 (3H, t, J= 7.12 Hz, CH_2CH_3), 1.34-1.68 (2H, m, CH_2CH_3), 1.87 (1H, bs, OH, deuterium oxide-exchangeable), 1.92-1.98 (1H, m, C_3H), 2.03-2.11 (1H, m, C_2H), 2.53 (1H, dd, J= 16.32 and 5.82 Hz, C_4H), 2.61 (1H, dd, J= 11.71 and 5.83 Hz, C_4H), 2.78-2.84 (2H, m, CH_2CN), 4.06 (3H, s, NCH_3), 4.81-4.87 (1H, m, C_1H), 7.13-7.21 (1H, m, aromatic proton) 7.23-7.32 (1H, m, aromatic proton), 7.42 (1H, d, J= 8.1 Hz, aromatic proton), 8.02 (1H, d, J= 8.2 Hz, aromatic proton); ms: m/z 269(20) $[M+1]^+$, 268(28) $[M]^+$, 251(16) $[M-OH]^+$, 238(25) $[M-CH_2O]^+$, 143(100) $[M-C_7H_{11}NO]^+$. *Anal.* Calcd. for $C_{17}H_{20}N_2O$: C, 76.08; H, 7.51; N, 10.44. Found: C, 76.03; H, 7.59; N, 10.39.

(3-Ethyl-1-hydroxy-9-methyl-4-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-2-yl)acetonitrile (9). To a solution of 1.5 g (5.60 mmoles) of **8** in 50 ml of tetrahydrofurane (90%) were added dropwise 2.54 g (11.20 mmoles) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in 20 ml of tetrahydrofurane at 0 ºC under nitrogen atmosphere. The reaction mixture was stirred for 3 hours at 0 ºC then the solution was pored into 250 ml of 10% potassium carbonate and extracted with ethyl acetate. The organic layer was dried with anhydrous magnesium sulfate, and the solvent was removed. The residue was purified by chromatography using silica gel and ethyl acetate. After the solvent was evaporated, the product was recrystallized from ether to afford 1.05 g (66%) of **9**, mp: 139-140 ºC; ir (potassium bromide): ν 3445 (OH), 2957 (CH), 2241 (CN), 1624 (C=O) cm^{-1}; ^1H nmr (deuteriodimethylsulfoxide): δ 1.13 (3H, t, J= 7.16 Hz, CH_2CH_3), 1.33-1.68 (2H, m, CH_2CH_3), 1.94-2.01 (1H, m, C_3H), 2.34-2.47 (1H, m, C_2H), 2.76-2.83 (2H, m, CH_2CN), 4.03 (3H, s, NCH_3), 4.92-5.03 (1H, m, C_1H), 5.24 (1H, bs, OH, deuterium oxide-exchangeable), 7.16-7.31 (2H, m, aromatic protons), 7.47 (1H, m, aromatic proton), 8.10 (1H, d, J= 8.1 Hz, aromatic proton); ms: m/z 283(1.7) $[M+1]^+$, 282(5.4) $[M]^+$, 253(11.6) $[M-C_2H_5]^+$, 225(34.4) $[M-C_3H_5O]^+$, 129(100) $[M-C_8H_{11}NO_2]^+$. *Anal.* Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.44; H, 6.41; N, 10.02.

12-Ethyl-6-hydroxy-7-methyl-1,2,3,4,5,6-hexahydro-1,5-methano-2-azocino[4,3-*b*]indole (10). A solution of 500 mg (1.77 mmoles) of **9** in 40 ml of ethanol was hydrogenated at room temperature for 5 days under 3 atmosphere in the presence of 50 mg platinum(IV) oxide using a Parr apparatus. The catalyst was removed by filtration through Celite, and the solvent was removed under reduced pressure. Then, the residue was chromatographed using neutral aluminum oxide and ethyl acetate-hexane (1:1). The solvent was removed and then the product was recrystallized from ether to afford 145 mg (30%) of **10**, mp: 227-228 ºC, ir (potassium bromide): ν 3420 (OH and NH) cm^{-1}; ^1H nmr (deuteriodimethylsulfoxide): δ 0.98 (3H, t, J= 7.21 Hz, CH_2CH_3), 1.49-1.60 (2H, m, CH_2CH_3), 1.62-1.70 (1H, m, CH), 1.74-1.83 (1H, m, CH), 1.88 (1H, bs, deuterium oxide-exchangeable), 1.90-2.08 (3H, m, CH and CH_2), 2.12-2.21 (1H, m, CH), 3.15 (1H, bs, deuterium oxide-exchangeable), 4.05 (3H, s, NCH_3), 4.42-4.53 (1H, m, C_6H), 4.64 (1H, d, J= 6.45 Hz, C_1H), 7.01-7.20 (2H, m, aromatic protons), 7.33 (1H, d, J= 7.38 Hz, aromatic proton), 7.49 (1H, d, J= 7.91 Hz, aromatic proton); ms: m/z 271(3.5) $[M+1]^+$, 270(7.2) $[M]^+$, 253(39.7) $[M-OH]^+$, 210(63.5) $[M-C_2H_6NO]^+$, 181(100) $[M-C_4H_{11}NO]^+$. *Anal.* Calcd. for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20; N, 10.36. Found; C, 75.51; H, 8.09; N, 10.40.

12-Ethyl-7-methyl-6-oxo-1,2,3,4,5,6-hexahydro-1,5-methano-2-azocino[4,3-*b*]indole(*N*-methylnordasycarpidone) (11). To a solution of 250 mg (0.92 mmole) of **10** in 25 ml of dichloromethane, 800 mg (9.2 mmoles) of active manganese (IV) oxide was added. The reaction mixture was stirred for 3 hours, filtered through Celite and the solvent removed under reduced pressure. Then, the residue was chromatographed using silica gel and chloroform-methanol (9:1). The solvent was removed and then the product was recrystallized from ether-hexane to afford 180 mg (73%) of **11** as a white solid, mp: 219-220 ºC, ir (potassium bromide): ν 3348(NH), 1642 (CO) cm^{-1}; ^1H nmr (deuterio chloroform): δ 1.01 (3H, t, J= 7.23 Hz, CH_2CH_3), 1.58-1.67 (2H, m, CH_2CH_3), 1.89-2.04 (2H, m, CH_2), 2.06-2.13 (1H, m, CH), 2.21-2.37 (2H, m, CH_2), 2.43-2.56 (1H, m, CH), 3.08 (1H, bs, NH, deuterium oxide-exchangeable), 4.01 (3H, s, NCH_3), 4.51 (1H, d, J= 6.21 Hz, C_1H), 7.11-7.28 (2H, m, aromatic protons), 7.44 (1H, d, J= 7.92 Hz, aromatic proton), 7.68 (1H, d, J= 8.01 Hz, aromatic proton); ms: m/z 269(22) $[M+1]^+$, 268(43.7) $[M]^+$, 267(36.4) $[M-H]^+$, 253(8.4) $[M-NH]^+$, 225(100) $[M-C_2H_5N]^+$, 197(34.6) $[M-C_3H_5NO]^+$. *Anal.* Calcd. for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44. Found; C, 76.05; H, 7.41; N, 10.47.

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