In conclusion, the results obtained from these studies show that benzeneselenenyl halides react quite differently with 3-keto steroids in ethyl acetate and that PhSeBr is useful for the preparation of α-bromo 3-keto steroids.

Experimental Section

Melting points (uncorrected) were obtained on a Fisher-Johns apparatus. NMR spectra were determined with a JEOL-90Q spectrometer. Infrared spectra were recorded with a Perkin-Elmer 281 spectrophotometer. High-resolution mass spectra were taken on LKB-9000.

General Bromination Procedure Using Br_2/HOAc. To a solution of 3-keto steroid (350 mg, 13 mmol) in glacial acetic acid (6 mL) was added a solution (4 mL, 1 M) of bromine in glacial acetic acid, dropwise with stirring, at room temperature for 1 h. The bromo 3-keto 5α-steroids crystallized out and were purified by recrystallization from acetone–hexane. For the bromo 3-keto 5β-steroids, the reaction mixture was poured over water and extracted with $CHCl_3$. The chloroform fraction was dried ($MgSO_4$), filtered, and evaporated to give a residue from which pure α-bromo 3-keto steroids were purified by preparative thin-layer chromatography using benzene–ethyl acetate (3:1).

General Procedure for Bromination of 3-Keto Steroids Using PhSeBr. To a solution of 3-keto steroid (390 mg, 14.2 mmol) in ethyl acetate (15 mL) was added PhSeBr (404 mg, 17.2 mmol). The reaction mixture was kept at room temperature for 1 h. Bromo 3-keto 5α-steroids crystallized out of the reaction mixture and were purified by recrystallization from acetone–hexane. Bromo 3-keto 5β-steroids were applied directly to a preparative TLC as described above.

2α-(Phenylselenenyl)-5α-estrane-3,17-dione (2). To a solution of 1 (390 mg, 14.2 mL) in ethyl acetate (15 mL) was added PhSeCl (330 mg, 17.2 mmol). The resulting red orange solution was stirred at room temperature until it turned pale yellow. Chromatography over silica gel (hexane) gave 230 mg (60%) of 2 as colorless crystals. Recrystallization from acetone–hexane gave an analytical sample: mp 184–185 °C; ^{1}H NMR ($CDCl_3$) δ 0.912 (s, 3 H, C-18 CH_3), 4.13 (dd, 1 H, J = 13.68, 5.70 Hz, C-2 H), 7.23–7.30 (m, 3 H), 7.50–7.59 (m, 2 H).

2α-Chloro-5α-estrane-3,17-dione (3). To a solution of 1 (110 mg) in HOAc (1.5 mL) was added freshly prepared *tert*-butyl hypochlorite[14] (0.04 mL) and warmed to 65 °C for 1 h.[15] The reaction mixture was kept at room temperature overnight to yield white crystalline material. Crystals were filtered, washed with MeOH, and recrystallized from MeOH to yield 83 mg of 3 (73%): mp 242–244 °C; IR (KBr) 1740 (17-ketone), 1729 (3-ketone) cm^{-1}; ^{1}H NMR δ 0.90 (s, 3 H, C-18 CH_3), 4.48 (dd, 1 H, J = 13.58, 5.70 Hz, C-2 H); mass spectrum, calcd for $C_{18}H_{25}ClO_2$ m/e 308.85175, found m/e 308.84935.

2-Chloro-5α-estr-1-ene-3,17-dione (5). To a solution of 2 (80 mg) in ethyl acetate (3 mL) was added PhSeCl (65 mg) and the reaction mixture stirred for 1 h. The ethyl acetate solution was extracted with two 3-mL portions of H_2O and cooled to 10 °C, at which time 0.04 mL of 30% H_2O_2 is added. An additional 0.02 mL of 30% H_2O_2 was added after 10 min and again after 20 min. After the mixture was stirred for an additional 40 min, 5-mL of H_2O was added and the ethyl acetate layer separated, washed, dried over $MgSO_4$, and evaporated to dryness. The reaction mixture was resolved on preparative TLC as described above to yield 30 mg (37%) of 2-chloro-5α-estr-1-ene-3,17-dione (5), mp 177–179 °C. NMR and IR were identical with those of the previously synthesized compound.[1]

2α-Bromo-5α-estrane-3,17-dione (7): yield 75% from Br_2/HOAc reaction and 66% from PhSeBr reaction; mp 234–235 °C; IR (KBr) 1740 (17-ketone), 1725 (3-ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3 H, C-18 CH_3), 4.64 (dd, 1 H, J = 13.63, 5.71 Hz, C-2 H); mass spectrum, m/e (relative intensity) 354 (M^+ + 1, 44), 352 (M^+ - 1, 41), 273 (M^+ - Br, 69), 255 (43), 203 (37), 185 (43), 147 (100), 108 (59), 91 (59); mass spectrum, calcd for $C_{18}H_{25}BrO_2$ m/e 353.30775, found m/e 353.30695.

2α-Bromo-5α-androstane-3,17-dione (9): 87% and 73% yields from Br_2/HOAc and PhSeBr reactions, respectively; mp 206–207 °C; NMR and IR were identical with those of an authentic sample of 9.

4β-Bromo-5β-androstane-3,17-dione (11): 79% and 65% yields from Br_2/HOAc and PhSeBr reactions, respectively; mp 192–194 °C; IR (KBR) 1740 (17-ketone), 1726 (3-ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 3 H, C-18 CH_3), 1.123 (s, 3 H, C-19 CH_3), 4.94 (d, 1 H, J = 11.5 Hz, C-4 H).

2β-Bromo-5β-androstane-3,17-dione (12). Reaction conditions were essentially similar to those used for bromination with PhSeBr described above except the time of reaction was increased from 1 to 96 h, which results in a mixture of 11 and 12 in a ratio of 1:5 based on NMR analysis. Recrystallization from acetone–hexane gave 45% yield of the analytical product: mp 198–199 °C; IR (KBr) 1740 (17-ketone) 1727 (3-ketone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 3 H, C-18 CH_3), 1.089 (s, 3 H, C-19 CH_3), 4.69 (dd, 1 H, J = 14.07, 5.72 Hz, C-2 H); mass spectrum, m/e (relative intensity) 369 (M^+ + 1, 74), 367 (M^+ + 1, 73), 288 (M^+ - Br, 100), 270 (67), 231 (45), 218 (84), 200 (51), 161 (69), 122 (44); mass spectrum, calcd for $C_{19}H_{27}BrO_2$ m/e 367.55174, found m/e 367.55196.

2α-Bromo-5β-estrane-3,17-dione (15): 86% and 84% yields were obtained from Br_2/HOAc and PhSeBr reactions, respectively; mp 186–188 °C; ^{1}H NMR δ 0.90 (s, 3 H, C-18 CH_3), 4.64 (q, 1 H, J = 4.2 Hz, C-2 H).

Registry No. 1, 5696-58-2; 2, 103304-60-5; 3, 103304-61-6; 5, 101366-71-6; 7, 103304-62-7; 8, 846-46-8; 9, 28507-01-9; 10, 1229-12-5; 11, 4588-83-4; 12, 18000-82-3; 13, 5696-51-5; 15, 102922-53-2.

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Palladium-Mediated Diazo Insertions: Preparation of 3-Alkyl-2-carbomethoxycyclopentenones

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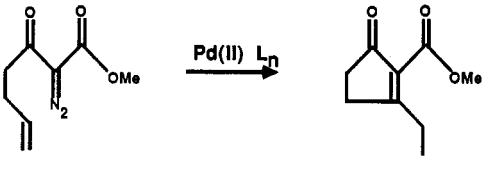
The development of new methods for carbocyclic ring formation is one of the abiding concerns of synthetic organic chemistry. We report a new method for the preparations of 3-alkyl-2-carbomethoxycyclopentenones, based on palladium(II)-mediated[3] cyclization of β-alkenyl α'-diazo ketones (1 → 2).[4,5]



1 2

We have briefly examined the scope of this reaction (Table I). While in general $PdCl_2$·$(PhCN)_2$[6] is effective

(1) Fellow of the Alfred P. Sloan Foundation, 1982–1987.
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(5) Lewis acid catalyzed rearrangement of β- and γ-alkenyl α'-diazo ketones to cyclopentenones has been reported. (a) Smith, A. B., III; Toder, B. H.; Branca, S. J.; Dieter, R. K. *J. Am. Chem. Soc.* **1981**, *103*, 1996. (b) Doyle, M. P.; Trudell, M. L. *J. Org. Chem.* **1984**, *49*, 1196. Similar acid-mediated cyclization of the diazoesters in Table I was attempted but was not successful.
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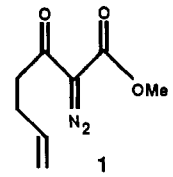
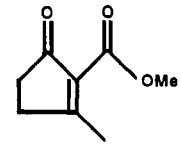
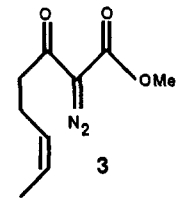
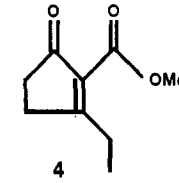
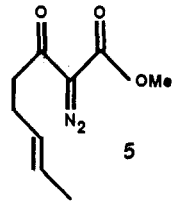
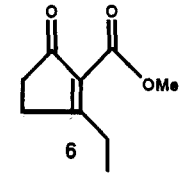
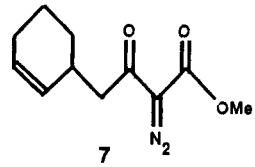
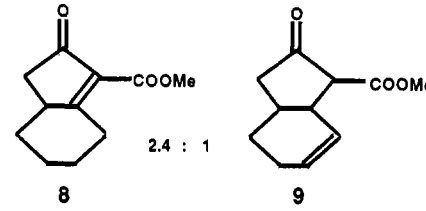
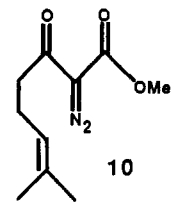
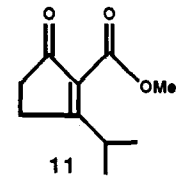
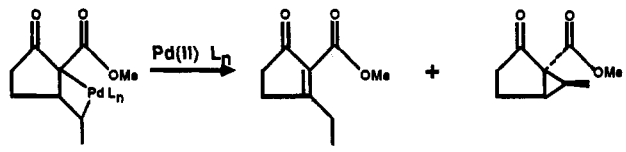
0022-3263/86/1951-3382$01.50/0

Table I

reacn	reactants	products	yield, %
1	 1	 2	55
2	 3	 4	34
3	 5	 6	46
4	 7	 8 2.4 : 1 9	73
5	 10	 11	53

in catalyzing the reaction, conditions for optimal yield of the enone vary considerably from substrate to substrate. It is thus appropriate to survey the range of conditions outlined in the Experimental Section to optimize a given cyclization. In all cases so far studied, the main competing reaction is intramolecular cyclopropanation.

The reaction is believed to proceed through a palladocyclobutane[3] which partitions to the enone or the cyclopropane. Such a mechanism would rationalize the 6,5-



3 4 4a

enone 8 as well as the unsaturated 6,5-product 9. It should be noted that this mechanism, predicated on β-hydride elimination, is conceptually related to the recent work of Trost.[7]

Experimental Section

General. ^1H NMR spectra were obtained on a Bruker AM-250 as solutions in $CDCl_3$. ^{13}C NMR spectra were obtained on a Bruker WM-250 as solutions in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference tetramethylsilane. The couplings (J) are in hertz (Hz). The infrared (IR) spectra were determined on a Unicam SP1100 spectrometer as solutions in CCl_4 and are reported in reciprocal centimeters (cm^{-1}). Mass spectra (MS) were taken at 70 eV on a du Pont 21-492B mass spectrometer and are reported as mass per unit charge (m/z), with intensities (as a percentage of the peak of greatest ion current having $m/z \geq 100$) in parentheses. Organic chemicals were purchased from Aldrich Chemical Co. Toluene was distilled over Na metal and stored over molecular sieves (4 Å). Acetonitrile was distilled over NaH and stored over molecular sieves (4 Å). Nitromethane was distilled over molecular sieves (4 Å) and stored over molecular sieves (4 Å). The extracting solvent used was a mixture of recovered organic solvents, including methylene chloride, ethyl acetate, and petroleum ether. The solvent mixtures used for chromatography are volume/volume mixtures. R_f values indicated refer to thin-layer chromatography on Analtech 2.5 × 10 cm, 250-μm analytical plates coated with silica gel GF. Column chromatography was carried out with TLC-mesh silica gel, following the procedure we have described.[8]

Preparation of 1. To a solution of 7.7 g (45 mmol) of the β-keto ester, prepared by the method of Weiler,[9] in 94 mL of acetonitrile at 25 °C were added 6.0 g (50 mmol) of mesyl azide[10] and 9.15 g (90 mmol) of triethylamine. The reaction mixture was stirred for 75 min. The solution was diluted with 10% aqueous NaOH and extracted with ether. The combined organic extracts were washed with saturated NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residual oil was divided into two portions. Each portion was chromatographed on 30 g of silica gel with 100

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mL of pure petroleum ether, 100 mL of 1% EtOAc/petroleum ether, and 200 mL of 3% EtOAc/petroleum ether. The first 50 mL was discarded. The next 350 mL was concentrated in vacuo to give a total of 8.44 g (95%) of the α-diazo β-keto ester as an oil: R_f (20% EtOAc/hexane) 0.80; ^{13}C NMR 191.9, 161.6, 128.5, 125.0, 51.9, 39.8, 21.7, 12.5; ^1H NMR (250 MHz, $CDCl_3$) 3.83 (s, 3 H), 2.90 (t, J = 7.3, 2 H), 2.73 (q, J = 6.6, 2 H), 1.62 (d, J = 6.6, 3 H); IR ($CHCL_3$) 3090, 3020, 2980, 2150, 1720, 1655, 1440, 1410, 1370, 1350, 1320, 1230, 1140, 1105, 1060, 1010, 995, 935, 880; MS, 196 (6), 153 (24), 149 (33), 136 (32), 121 (27), 109 (26), 108 (51), 101 (24), 95 (77).

Preparation of 2. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and charged with 5 mg (0.01 mmol) of $PdCl_2(PhCN)_2$. Ester **1** (338 mg, 1.85 mmol, in 3.7 mL CH_3CN) was added via syringe. 2,2'-Azobis(2-methyl-propionitrile) (34 mg, 0.21 mmol, 10% by weight) was then added. The mixture was magnetically stirred at reflux for 3 h. The reaction mixture was allowed to cool and evaporated directly onto 0.5 g of 60–200 mesh silica gel. The absorbed mixture was added to the top of a 10-g column.[8] The column was then eluted with 50-mL portions of 3–10% acetone/petroleum ether, in 1% increments. The first 280 mL was discarded. The next 160 mL was concentrated in vacuo to give 158 mg (1.02 mmol, 55%) of **2** as a clear yellow oil: R_f (20% acetone/hexane) 0.22; ^{13}C NMR 19.4 (q), 32.8 (t), 35.0 (t), 51.8 (q), 132.3 (s), 163.7 (s), 185.6 (s), 203.5 (s); ^1H NMR 2.4 (s, 3 H), 2.5 (t, J = 5.0, 2 H), 2.7 (t, J = 5.0, 2 H), 3.85 (s, 3 H); IR 2983, 1754, 1721, 1638, 1553, 1442, 1341, 1293, 1254, 1232, 1145, 1062, 1012, 974; MS, 154.063 (31), 123 (100), 122 (43), 96 (46), 95 (40).

Preparation of 4. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and changed with 7 mg (0.02 mmol) of $PdCl_2(PhCN)_2$. Ester **4** (268 mg, 1.37 mmol) was added in 2.7 mL of toluene via syringe. The mixture was refluxed for 5 h, then allowed to cool, and evaporated directly onto 0.5 g of 60–200 mesh silica gel. The absorbed mixture was added to the top of a 20-g silica gel column. The column was eluted with 50-mL portions of 3–11% acetone/petroleum ether, in 1% increments. The first 100 mL was discarded. The next 150 mL was concentrated in vacuo to give 33.2 mg (0.19 mmol, 14%) of cyclopropane **4a** as an oil: R_f (20% acetone/hexane) 0.30; ^{13}C NMR 207.7 (s), 169.5 (s), 52.2 (q), 42.8 (s), 39.3 (t), 38.2 (d), 29.3 (d), 17.0 (t), 8.7 (q); ^1H NMR 3.75 (s, 3 H), 2.7–1.85 (m, 6 H), 1.2 (d, 3 H); IR 3060, 2980, 1750, 1725, 1460, 1415, 1320, 1250, 1110, 1040, 985; MS, 168 (30), 140 (30), 137 (92), 136 (57), 126 (44), 109 (35), 108 (39), 81 (64), 79 (49), 69 (32), 59 (100), 41 (57). The following 120 mL was concentrated in vacuo to give 78.0 mg (0.41 mmol, 34.0%) of enone **4** as a clear yellow oil, identical with **6** prepared below.

Preparation of 6. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and charged with 7 mg (0.02 mmol) of $PdCl_2(PhCN)_2$. Ester **5** (191.1 mg, 0.97 mmol) was added in 1.93 mL of toluene via syringe. The mixture was refluxed for 3 h, then allowed to cool, and evaporated directly onto 0.3-g of 60–200 mesh silica gel. The absorbed mixture was added to the top of a 10-g silica gel column. The column was eluted with 50-mL portions of 3–11% acetone/petroleum ether, in 1% increments. The first 250 mL was discarded. The next 120 mL was concentrated in vacuo to give 76 mg (0.45 mmol, 46%) of **6** as a clear yellow oil: R_f (20% acetone/hexane) 0.25; ^{13}C NMR 11.9 (q), 25.9 (t), 29.9 (t), 34.9 (t), 51.9 (q), 131.8 (s), 163.8 (s), 190.0 (s), 203.8 (s); ^1H NMR 1.21 (t, J = 7.6, 3 H), 2.50 (t, J = 4.9, 2 H), 2.72 (t, J = 4.9, 2 H), 2.82 (q, J = 7.6, 2 H), 3.85 (s, 3 H); IR 2982, 2362, 1752, 1722, 1627, 1550, 1462, 1437, 1344, 1292, 1224, 1202, 1150, 1020, 1000, 977; MS, 168.079 (30), 137 (72), 136 (100), 108 (32), 81 (38).

Preparation of 8 and 9. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and charged with 4.3 mg (0.01 mmol) of $PdCl_2(PhCN)_2$, 237 mg (2.5 mmol) of $LiBF_4$, and 1 mL of CH_3NO_2. The mixture was magnetically stirred at reflux for 1 h. Ester **7** (291 mg, 1.3 mmol) in 1.6 mL of CH_3NO_2 was added via syringe, followed by 3 mg of methylene blue. The reaction mixture was allowed to stir an additional hour at reflux. The mixture was allowed to cool to room temperature and then was quenched with distilled H_2O. Extracting solvent was added, and the two layers were separated. The aqueous layer was extracted four times with extracting solvent (25-mL portions). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was evaporated directly onto 2 g of 60–200 mesh silica gel. The absorbed mixture was added to the top of a 10-g silica gel column. The column was then eluted with 50-mL portions of 3–9% acetone/petroleum ether in 1% increments. The first 100 mL was discarded. The following 48 mL was concentrated in vacuo to give 55.4 mg (0.29 mmol, 22%) of **9** as a light yellow oil. The next 140 mL was discarded. The following 120 mL was concentrated in vacuo to give 130 mg (0.67 mmol, 51%) of **8** as a light yellow oil.

8: R_f (20% acetone/hexane) 0.29; ^{13}C NMR 25.1 (t), 27.0 (t), 30.1 (t), 35.2 (t), 41.0 (t), 42.0 (d), 51.8 (q), 129.3 (s), 163.7 (s), 190.6 (s), 202.6 (s); ^1H NMR 3.8 (s, 3 H), 3.5 (br d, J = 13.4, 1 H), 2.5–2.9 (m, 2 H), 1.1–2.4 (m, 8 H); IR 2962, 1752, 1722, 1634, 1554, 1450, 1438, 1360, 1322, 1299, 1274, 1240, 1230, 1160, 1020, 980; MS, 194.094 (40), 163 (67), 162 (100), 134 (80), 106 (39), 95 (69).

9: R_f (20% acetone/hexane) 0.52; ^{13}C NMR 23.5 (t), 25.0 (t), 32.1 (d), 39.6 (d), 44.4 (t), 52.5 (q), 59.8 (d), 127.1 (d), 128.6 (d), 169 (s), 211 (s); ^1H NMR 5.6–6.0 (m, 2 H), 3.8 (s, 3 H), 3.1 (m, 1 H), 1.1–2.7 (m, 8 H); IR 2952, 1759, 1732, 1552, 1253, 1220, 1003, 975; MS, 194.096 (18), 162 (35), 140 (35), 135 (100), 116 (34), 108 (33), 107 (30), 106 (34).

Preparation of 11. A flame-dried, two-necked, 25-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen purge was flushed with N_2 and charged with 5.1 mg (0.01 mmol) of $PdCl_2(PhCN)_2$, 196 mg (2.1 mmol) of $LiBF_4$, and 1 mL of toluene. The mixture was magnetically stirred at reflux for 1.5 h. Ester **10** (218.8 mg, 1.04 mmol) in 1.1 mL of toluene was added via syringe. The reaction mixture was allowed to stir an additional 15 min at reflux. The mixture was allowed to cool to room temperature and evaporated directly onto 0.5 g of 60–100 mesh silica gel. The absorbed mixture was added to the top of a 10-g column. The column was eluted with 50-mL portions of 2–12% acetone/petroleum ether, in 1% increments. The first 320 mL was discarded. The next 140 mL was concentrated in vacuo to give 101 mg (0.56 mmol, 53%) of **11** as a light yellow oil: R_f (20% acetone/hexane) 0.30; ^{13}C NMR 204.1 (s), 192.5 (s), 164.0 (s), 131.4 (s), 51.9 (q), 34.6 (t), 30.4 (d), 25.7 (t), 20.6 (q); ^1H NMR 3.85 (s, 3 H), 3.5–3.7 (m, 1 H), 2.66 (t, J = 2.0, 8, 2 H), 2.48 (t, J = 2.0, 2 H), 1.20 (d, J = 6.9, 6 H); IR 2994, 1722, 1626, 1555, 1437, 1549, 1494, 1253, 1236, 1172, 1146, 1022; MS, 182.0943 (16), 151 (52), 150 (100), 135 (36), 122 (36).

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Registry No. **1**, 62344-19-8; **2**, 23260-43-7; **3**, 62344-21-2; **4**, 103191-92-0; **5**, 62344-22-3; **7**, 103191-93-1; **8**, 103191-94-2; **9**, 103191-95-3; **10**, 62344-23-4; **11**, 103191-96-4; $PdCl_2(PhCN)_2$, 14220-64-5; $H_2C{=}CH(CH_2)_2COCH_2CO_2CH_3$, 30414-57-4.

Synthesis of Labeled (±)-2-Amino-3-butenoic Acids

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L-2-Amino-3-butenoic acid (L-vinylglycine, **1**), a naturally occurring unsaturated amino acid isolated from mush-

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