Chemical Studies on New Stemona Alkaloids, IV. Studies on New Alkaloids from Stemona tuberosa

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CHEMICAL STUDIES ON NEW *STEMONA* ALKALOIDS, IV.[1] STUDIES ON NEW ALKALOIDS FROM *STEMONA TUBEROSA*

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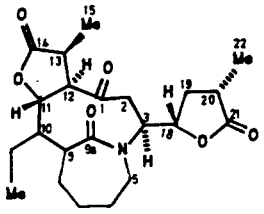
ABSTRACT.—Four new alkaloids, tuberostemonone [**1**], tuberostemonol [**2**], stemoamide [**3**], and tuberostemospironine [**4**], together with two known alkaloids, tuberostemonine and didehydrotuberostemonine, were isolated from the roots of *Stemona tuberosa* (Stemonaceae). Their structures were elucidated by ir, ms, and 1D- and 2D-nmr techniques including difference nOe spectra and homonuclear and heteronuclear spectral analyses.

The roots of *Stemona tuberosa* Lour. and related *Stemona* species (Stemonaceae) are used in Chinese traditional medicine as anticough agents and insecticides. Eleven alkaloids have been isolated from the roots so far; the structures of five were determined by X-ray analyses, and the structures of stemotinine and isostemotinine were first determined by us with spectral analyses (1). On this basis a series of new *Stemona* alkaloids have been discovered, and their structures were elucidated by 2D nmr techniques (2, 4, 5, 7–9). As a part of continuing studies on *Stemona* plants, we report four new alkaloids, tuberostemonone [**1**], tuberostemonol [**2**], stemoamide [**3**], and tuberostemospironine [**4**] together with two known alkaloids, tuberostemonine [**5**] and didehydrotuberostemonine [**6**] separated from *S. tuberosa* collected in Guangdong Province, China.

Tuberostemonone [**1**], mp 208–209°, $[\alpha]^{8}D$ +134.8° (c = 0.1, $CHCl_3$), in hrms showed the molecular formula as $C_{22}H_{31}NO_6$, with eight degrees of unsaturation. The strong ir absorptions at 1788, 1775, 1715, 1638, 1190, and 1175 cm^{-1} as well as the ^{13}C-nmr carbonyl region signals at δ 178.18 (s), 178.08 (s), 205.00 (s), and 176.57 (s) suggested the presence of two saturated γ-lactones, a ketone, and a lactam. The characteristic ms base peak at *m/z* 306 $[M-C_5H_7O_2]^+$ indicated the presence of an α-methyl-γ-lactone ring annexed to the C-3 of a pyrrolidine ring (1). The presence of the common ddd signals of the H-3 at δ 5.37 and the geminal CH_2-5 at δ 3.51 and 3.81 indicated that the lactam carbonyl could be proposed at C-9a. This suggested that the C-1–C-9a bond of the perhydroazaazulene ring, common in the *Stemona* alkaloids, was most probably broken via biosynthesis in the plant. The ketone carbonyl was located at C-1 due to the downfield shift of the typical CH_2-2 geminal signals at δ 2.39 (dd, J = 3.7, 12.2, H-2α), 3.19 (dd, J = 12.2, 12.2, H-2β) and the H-12 at δ 3.56 (dd, J = 7.7, 9.9). In the ^1H-^1H COSY spectrum, the cross peaks among H-11 (δ 5.08, dd, J = 7.1, 9.9), H-12, H-13 (δ 2.91, dq, J = 7.0, 7.7) as well as Me-15 (δ 1.30, d, J = 7.0) located the structure of the second γ lactone. Thus, the entire structure was suggested as **1**. The relative configuration was proposed on the basis of nOe difference spectra and J values in combination with the Karplus equation. Considering the biogenetic relationships in the *Stemona* alkaloids, the C-22 methyl of the γ-lactone ring annexed to C-3 usually shows α orientation. In addition, irradiation of protons at δ 4.46 (H-18) led to 5.3% and 3.9% enhancement of protons at δ 2.72 (H-20) and δ 2.48 (H-19β), respectively, while H-3 had no response. Moreover, irradiation of H-13 (δ 2.91) produced 2.4% enhancements at H-12 (δ 3.56) and 3.8% at H-10 (δ 2.32) but not at H-11 (δ 5.08), whereas H-12 of tuberostemonine was in a β orientation. Therefore, the relative configuration of **1** was established; it was further confirmed by

[1]For part III, see W.-H. Lin, Y. Ye, and R.S. Xu, *Youji Huaxue*, **11**, 500 (1991).



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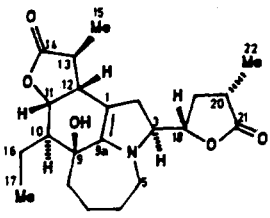

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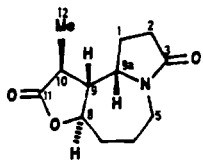

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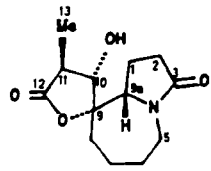

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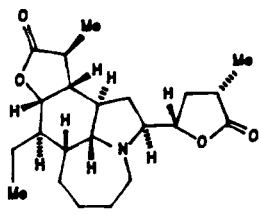

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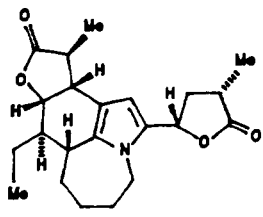

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X-ray analysis (2). The ^{1}H- and ^{13}C-nmr data were assigned as in Tables 1 and 2 on the basis of ^{13}C-^{1}H COSY spectral analyses.

Tuberostemonol [**2**], amorphous, $[\alpha]^{20}D$ +33.54° (c = 0.3, MeOH), showed the

TABLE 1. ^{1}H-nmr Spectral Data for Alkaloids **1–4**.[a]

Proton	δ (ppm)	J (Hz)	Proton	δ (ppm)	J (Hz)
		1			
H-2α . .	2.39 (dd)	12.2 (2β), 3.7 (3α)	H-12 . .	3.56 (dd)	9.9 (11β), 7.7 (13α)
H-2β . .	3.19 (dd)	12.2 (2α), 12.2 (3α)	H-13 . .	2.91 (dq)	7.7 (12α), 7.0 (15-Me)
H-3 . . .	5.37 (ddd)	3.7 (2α), 12.2 (2β), 5.7 (18β)	H-14 . .		
			H-15 . .	1.30 (d)	7.0 (13α)
H-5α . .	3.81 (ddd)	12.1 (5β), 2.9 (6α), 9.2 (6β)	H-16 . .	1.80 (m)	
				1.27 (m)	
H-5β . .	3.51 (ddd)	12.1 (5α), 2.6 (6α), 4.6 (6β)	H-17 . .	0.94 (d)	7.2 (16), 7.4 (16)
			H-18 . .	4.46 (ddd)	5.7 (3α), 5.7 (19β), 10.9 (19α)
H-6α . .	1.91 (m)				
H-6β . .	1.77 (m)		H-19α .	1.78 (m)	
H-7α . .	1.51 (m)		H-19β .	2.48 (ddd)	5.7 (18β), 11.2 (19α), 5.5 (20β)
H-7β . .	1.75 (m)				
H-8α . .	1.70 (m)		H-20 . .	2.72 (m)	
H-8β . .	1.52 (m)		H-21 . .		
H-9 . . .	3.08 (ddd)	1.8 (8α), 11.0 (8β), 9.2 (10α)	H-22 . .	1.23 (d)	7.1 (20)
H-9a . . .					
H-10 . . .	2.32 (m)				
H-11 . . .	5.08 (dd)	7.1 (10α), 9.9 (12α)			

TABLE 1. Continued.

Proton	δ (ppm)	*J* (Hz)	Proton	δ (ppm)	*J* (Hz)
		2			
H-2α . .	1.99 (dd)	13.0 (2β), 5.5 (3α)	H-12 . .	2.67 (dd)	8.0 (11β), 11.6 (13α)
H-2β . .	1.39 (dd)	13.0 (2α), 10.7 (3α)	H-13 . .	2.26 (dq)	11.6 (12α), 7.0 (15-Me)
H-3 . . .	3.49 (ddd)	5.5 (2α), 10.7 (2β) 7.8 (18)	H-14 . .		
H-5α . .	2.48 (ddd)	12.0 (5β), 2.0 (6α) 12.0 (6β)	H-15 . .	1.30 (d)	7.0 (13α)
H-5β . .	2.58 (ddd)	12.0 (5α), 5.5 (6α) 5.5 (6β)	H-16 . .	1.72 (m) 1.36 (m)	
H-6 . . .	1.82 (m) 1.56 (m)		H-17 . .	0.99 (t)	7.6 (16)
H-7 . . .	2.00 (m) 2.10 (m)		H-18 . .	4.43 (ddd)	7.8 (3α), 7.5 (19α) 7.3 (19β)
H-8 . . .	1.82 (m) 1.56 (m)		H-19α .	2.15 (ddd)	13.2 (19β), 9.0 (20β) 7.5 (18β),
H-9 . . .			H-19β .	1.93 (ddd)	13.2 (19α), 7.3 (18β) 5.5 (20β),
H-9a . . .			H-20 . .	2.67 (ddq)	5.5 (19β), 9.0 (19α) 7.5 (22-Me),
H-10 . . .	2.09 (m)		H-21 . .		
H-11 . . .	4.67 (dd)	11.2 (10α), 8.0 (12α)	H-22 . .	1.29 (d)	7.5 (20β),
		3			
H-1 . . .	1.93 (m) 1.61 (m)		H-8 . . .	4.09 (ddd)	2.9 (7α), 10.2 (7β), 11.1 (9β)
H-2 . . .	2.32 (m)		H-9 . . .	2.29 (ddd)	11.1 (8α), 12.4 (10α) 6.4 (9aβ)
H-5α . .	2.55 (ddd)	14.2 (5β), 12.5 (6β) 1.5 (6α)	H-9a . .	3.88 (ddd)	6.4 (9β), 11.1 (1α) 6.3 (1β)
H-5β . .	4.01 (ddd)	14.2 (5α), 4.7 (6α) 2.1 (6β)	H-10 . .	2.48 (dq)	12.4 (9β), 6.7 (12-Me)
H-6 . . .	1.75 (m) 1.41 (m)		H-11 . .		
H-7 . . .	1.62 (m)		H-12 . .	1.18 (d)	6.7 (10α)
		4			
H-1α . .	1.90 (m)		H-8 . . .	1.57 (m)	
H-1β . .	2.01 (m)				
H-2α . .	2.24 (m)		H-9 . . .		
H-2β . .	2.25 (m)				
H-3 . . .			H-9a . .	3.70 (dd)	6.4 (1β), 9.8 (1α)
H-5α . .	2.80 (ddd)	13.2 (5β), 12.7 (6β) 1.0 (6α)	H-10 . .	3.77 (d)	10.2 (11α)
H-5β . .	3.83 (ddd)	13.2 (5α), 3.6 (6α) 2.9 (6β)	H-11 . .	2.49 (dq)	10.2 (10β), 7.0 (13-Me)
H-6 . . .	1.65 (m) 1.29 (m)		H-12 . .		
H-7 . . .	1.51 (m) 1.90 (m)		H-13 . .	1.15 (d)	7.0 (11α)

*In $CDCl_3$.

TABLE 2. ^{13}C-nmr Spectral Data for Alkaloids **1**—**4**.[a]

Carbon	Compound			
	1	**2**	**3**	**4**
C-1	205.00 (s)	114.0 (s)	30.43 (t)	28.66 (t)
C-2	44.56 (t)	37.8 (t)	34.84 (t)	29.95 (t)
C-3	56.25 (d)	65.4 (d)	173.83 (s)	175.08 (s)
C-5	39.67 (t)	54.6 (t)	40.00 (t)	41.17 (t)
C-6	23.71 (t)	30.8 (t)	22.31 (t)	20.64 (t)
C-7	21.09 (t)	28.0 (t)	25.45 (t)	21.49 (t)
C-8	26.06 (t)	32.1 (t)	77.45 (d)	25.85 (t)
C-9	51.47 (d)	130.0 (s)	52.50 (d)	87.52 (s)
C-9a	176.57 (s)	121.1 (s)	55.85 (d)	67.59 (d)
C-10	44.56 (d)	48.8 (d)	37.12 (d)	78.29 (d)
C-11	79.41 (d)	82.7 (d)	177.21 (s)	40.41 (d)
C-12	59.78 (d)	51.9 (d)	13.87 (q)	175.40 (s)
C-13	39.67 (d)	36.6 (d)		11.86 (q)
C-14	178.18 (s)[b]	179.2 (s)[b]		
C-15	15.15 (q)	16.8 (q)		
C-16	18.87 (t)	26.4 (t)		
C-17	12.16 (q)	11.5 (q)		
C-18	77.01 (d)	79.5 (d)		
C-19	34.10 (t)	32.7 (t)		
C-20	35.50 (d)	34.1 (d)		
C-21	178.8 (s)[b]	179.3 (s)[b]		
C-22	14.79 (q)	16.2 (q)		

[a]In $CDCl_3$.
[b]Exchangeable.

formula $C_{22}H_{31}NO_5$ based on elemental analyses and eims. The presence of two γ lactones, an olefinic bond, and a hydroxyl group were deduced from the ir absorptions (3470, 1770, 1760, 1650, and 1180 cm^{-1}) and were supported by ^{13}C-nmr signals [δ 179.3 (s), 179.2 (s), 121.1 (s), 114.0 (s), and 130.0 (s)]. The characteristic ms base peak at *m/z* 290 $[M - C_5H_7O_2]^+$ indicated an α-methyl-γ-lactone ring annexed to C-3 of the azaazulene ring. The similarity of its ir and ^{1}H nmr suggested that the structure belongs to the tuberostemonine (3) type of skeleton. In the ^{1}H-^{1}H COSY spectrum, **2** showed cross peaks among H-12 (δ 2.67, dd, $J = 8.0$, 11.6), H-11 (δ 4.67, dd, $J = 11.2$, 8.0), and H-13 (δ 2.26, dq, $J = 7.0$, 11.6), and the lack of H-9a and H-1 signals indicated that the olefinic double bond was located between their carbons. The correlation of proton signals of H-10 (δ 2.09, m) with the adjoining protons of H-11 and CH_2-16 (δ 1.72, m; δ 1.36, m) predicted that the hydroxyl group was most probably substituted at C-9. This was also supported by the downfield-shifted quaternary carbon signal of C-9 [δ 130.0 (s)]. The other signals as typical ddd signals of H-3 (δ 3.49) and CH_2-5 geminal (δ 2.48 and 2.58), as well as proton signals at C-6, C-7, and C-8, suggested that the azaheptcyclo ring kept a stable chair conformation, and β orientation of the OH group at C-9 was assigned. NOe's of 7.5%, 2.0%, and 1.5% were observed at H-12, Me-15, and Me-17 upon irradiation of H-11; this suggested that H-11, H-12, Me-15, and the ethyl were in the normal β orientation. That no response was observed at H-18 upon irradiation of H-3 suggested that H-3 and H-18 were trans 3α and 18β. Irradiation of H-18 produced 2.1% enhancement at H-20, so Me-22 was in an α orientation. On this basis the relative configuration was deduced as **2**. The ^{1}H- and ^{13}C-nmr data for **2** were assigned as in Tables 1 and 2.

Stemoamide [**3**], amorphous, $[\alpha]^{21.6}D$ −28.1° (c = 0.125, MeOH), had a molecular formula of $C_{12}H_{17}NO_3$ according to hrms. The ir absorptions at 1750 and 1664 cm^{-1}, in combination with ^{13}C-nmr signals at δ 177.21 (s) and 173.83 (s), proposed the presence of a γ lactone and a lactam ring. The lactam carbonyl was assigned at C-3 because of the presence of the characteristic geminal signals of CH_2-5 (δ 4.01, ddd, J = 2.1, 4.7, 14.2, H-5β; δ 2.55, ddd, 1.5, 12.5, 14.2, H-5α) together with the cross peaks of the perhydroazaazulene ring in the ^1H-^1H COSY. The correlation among H-9 (δ 2.29, ddd, J = 6.4, 11.1, 12.4), H-9a (δ 3.88, ddd, J = 6.3, 6.4, 11.1), and H-10 (δ 2.48, dq, J = 6.7, 12.4) in the ^1H-^1H COSY spectrum suggested that the γ lactone ring was connected to the perhydroazaazulene ring at C-8 and C-9, and in turn, the Me group (δ 1.18, d, J = 6.7, Me-12) was located at C-10. The structure and the relative configuration of **3** were also suggested by comparison of proton signals and J values with those of stemoninine (4). Compound **3** is also one of the several C-3 lactam-type *Stemona* alkaloids (5) that we have found in these plants. The ^1H- and ^{13}C-nmr data for **3** were assigned as in Tables 1 and 2.

The molecular formula for tuberostemospironine [**4**], mp 245–246°, $[\alpha]^{16}D$ −30° (c = 0.02, MeOH), was established as $C_{13}H_{19}NO_4$ based on elemental analyses and eims. This formula required five degrees of unsaturation. The ir absorptions (3345, 1775, 1665 cm^{-1}) in association with ^{13}C-nmr signals [δ 175.40 (s), 175.08 (s)], suggested the presence of a γ lactone, a lactam, and a hydroxyl group. The ^1H-^1H COSY analyses predicted that the lactam carbonyl was also placed at C-3 by comparing the ^1H-nmr signals of CH_2-5 and H-9a with those of **3**. The vicinal correlation of the H-9a (δ 3.70, dd, J = 6.4, 9.8) with the geminal CH_2-1 signals (δ 1.90, m; 2.01, m), absence of the γ proton in the γ lactone ring, and the presence of a quaternary carbon signal at δ 87.52 suggested a spiro-ring at C-9 of the perhydroazaazulene ring. The downfield shifted H-10 (δ 3.77, d, J = 10.2), its correlation with the H-11 (δ 2.49, dq, J = 10.2, 7.0), and correlation of H-11 with the Me-13 (δ 1.15, d, J = 7.0) indicated that the hydroxyl group was substituted at C-10. The spiro configuration of the γ lactone was confirmed by the NOESY cross peaks between H-10 and Me-13, H-11 and H-1α, and OH and H-1α, and the relative configuration of this structure was established as **4**. Further spectral analyses led to the assignment of the ^1H- and ^{13}C-nmr data as in Tables 1 and 2.

The structure of tuberostemonine [**5**] was identified by comparing with an authentic sample (6), and didehydrotuberostemonine [**6**] was identified by direct comparison of physical and chemical data with those obtained from the oxidation products from tuberostemonine according to known methods (3).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were determined on a Kofler mp apparatus and were uncorrected. The ir spectra were recorded on a Perkin-Elmer 559B spectrophotometer. The hrms and eims data were collected on an MAT-711 spectrometer. ^1H-nmr, ^{13}C-nmr, 2D homo- and heteronuclear correlated spectra as well as nOe experiments were recorded on a Bruker AM-400 and an AM-100 nmr spectrometer [in $CDCl_3$, CD_3OD, $(CD_3)_2CO$, and C_5D_5N with TMS as an internal standard]. Si gel used for flash chromatography was produced in the Qindao Marine Chemical Industrial Factory. The following solvent systems were applied for Si gel tlc: petroleum ether-Me_2CO (2:1), MeOH-$CHCl_3$ (95:5), and *n*-hexane–Me_2CO (1:1), and the compounds were detected by spraying with Dragendorff's reagent.

PLANT MATERIAL.—The roots of *S. tuberosa* were obtained from a local distributor of Medicinal Material in Mai County, Guangdong Province, southern China, and identified by Prof. X.S. Bao, Shanghai Institute for Drug Control. An herbarium sample has been deposited in the South China Institute of Botanica, Academia Sinica.

ISOLATION AND SEPARATION.—The roots (25 kg) were ground and percolated with 95% EtOH. After evaporation of the collected percolate, the crude extract was acidified with dilute HCl (4%) and filtered. The filtrate was basified with aqueous NH_3 and extracted with Et_2O to afford 35 g of crude al-

kaloid. Part of the HI salt (10.0 g) of tuberostemonine was crystallized in cubic form when the mixture was treated with HI in Me_2CO. The mother liquor was basified and extracted with $CHCl_3$ to yield 12.0 g of residue, which was further chromatographed on Si gel and eluted with a gradient C_6H_6/EtOAc to obtain didehydrotuberostemonine (1.50 g) and tuberostemonone [**1**] (90 mg). The remaining fractions were collected and rechromatographed on an Al_2O_3 column with Et_2O as eluent to obtain stemoamide [**3**] (8 mg). The remaining fractions were purified on preparative tlc to obtain tuberostemonol [**2**] (11 mg) and tuberostemospironine [**4**] (10 mg).

Tuberostemonone [**1**].—Colorless cubes (Me_2CO): mp 208–209°; $[\alpha]^{8}D$ +134.8° (c = 0.1, $CHCl_3$); ir ν max (KBr) 2940, 1788, 1775, 1715, 1638, 1460, 1410, 1333, 1190, 1170, 1100, 1000 cm^{-1}; hrms *m/z* $[M]^+$ 405.2138 (calcd for $C_{22}H_{31}NO_6$, 405.2150); eims *m/z* $[M]^+$ 405, $[M-C_5H_7O_2]^+$ 306, 278, 264, 250, 166; ^1H nmr see Table 1; ^{13}C nmr see Table 2.

Tuberostemonol [**2**].—Amorphous: $[\alpha]^{20}D$ +33.54° (c = 0.3, MeOH); $C_{22}H_{31}NO_5$ (found C 66.50, H 7.72, N 3.53%; calcd C 67.86, H 7.97, N 3.60); ir ν max (KBr) 3470 (OH), 2915, 1770, 1760, 1650, 1460, 1380, 1320, 1180, 1000 cm^{-1}; eims *m/z* $[M-18]^+$ 371, 290, 272, 244, 198, 149; ^1H nmr see Table 1; ^{13}C nmr see Table 2.

Stemoamide [**3**].—Amorphous: $[\alpha]^{21.6}D$ −28.1° (c = 0.125, MeOH); ir ν max (KBr) 2920, 1750, 1664, 1455, 1390, 1325, 1255, 1160, 1125, 1045, 982 cm^{-1}; hrms *m/z* $[M]^+$ 223.1211 (calcd for $C_{12}H_{17}NO_3$, 223.1207); eims *m/z* $[M]^+$ 223, 208, 194, 149, 125, 124; ^1H nmr see Table 1; ^{13}C nmr see Table 2.

Tuberostemospironine [**4**].—Colorless cubes (Me_2CO): mp 245–246°; $[\alpha]^{16}D$ −30° (c = 0.02, MeOH), $C_{13}H_{19}NO_4$ (found C 61.68, H 7.63, N 5.44; calcd C 61.66, H 7.51, N 5.53); ir ν max (KBr) 3345, 2975, 2940, 2880, 1775, 1665, 1460, 1431, 1382, 1310, 1200, 1115, 980, 960, 890, 750, 650 cm^{-1}; eims *m/z* $[M]^+$ 253, 237, 222, 208, 180, 171, 152, 150, 138, 136, 124; ^1H nmr see Table 1; ^{13}C nmr see Table 2.

Tuberostemonine [**5**].—Colorless needles (EtOH): mp 86–88° [lit. (6) 84–88°], $[\alpha]^{21}D$ −25.40° (c = 0.059, Me_2CO). Identified by comparison of tlc, ^1H nmr, and ^{13}C nmr with an authentic sample. Mmp showed no decrease: eims *m/z* $[M]^+$ 375, 344, 290, 276, 232, 218, 200, 172, 148, 134.

Didehydrotuberostemonine [**6**].—Colorless needles (Et_2O): mp 176–178° [lit. (7) 172–174°]; $[\alpha]^{8}D$ +105.96° (c = 0.1, C_6H_6); ir ν max (KBr) 2915, 2875, 1770, 1760, 1505, 1453, 1440, 1370, 1340, 1185, 1160, 1045, 1000, 920, 886 cm^{-1}; eims *m/z* $[M]^+$ 371, 327, 298, 272, 228, 216, 198, 174, 168, 134.

DEHYDRATION OF TUBEROSTEMONINE.—Tuberostemonine (10 mg) in 2 ml Me_2CO was reacted with 10 mg of fresh Ag_2O at 40°. The mixture was stirred overnight and filtered, and 4 mg of didehydrotuberostemonine was obtained after preparative tlc.

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