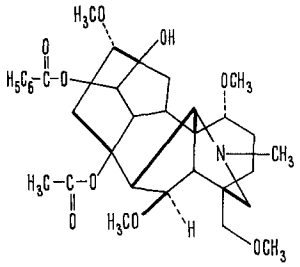
STUDIORUM PROGRESSUS

The Total Synthesis of Delphinine: A Stereoselective Synthesis of an Advanced Relay Compound*

Some twelve years ago we have deduced the structure **1** for the alkaloid delphinine[1]. Among various degradative studies which led to this structure proposal, a simple and comparatively high yield conversion of delphinine **1** to the 'aromatization product' **2** was discovered[2]. It is clear that **2** and its hydrolysis product **3** constitute an extremely favorable and advanced relay for the synthesis of delphinine. We wish to describe in the present communication a stereoselective total synthesis of compounds **2**, **3** and **4** and the rigorous identification of the synthetic materials with the corresponding 'natural' delphinine derivatives. The methoxy tetralone **5**[3] was converted to the allyl tetralone **6** [bp 118–120°/0.05 mm Hg; $m/e = 216$][4] by the STORK[5] pyrrolidine-enamine procedure. Compound **6** was stirred in benzene solution at 60 °C with a slight excess of sodium hydride under nitrogen. After cooling below 20 °C a small excess of benzyl chloromethyl ether[6] was added and the stirring continued for 18 h. The pure geminally substituted product **7** [NMR: singlet (2H) $\tau = 5.7$ ppm (benzylic methylene); $m/e = 336$] was isolated by chromatography on silica gel in a yield of 68% as a colorless oil.



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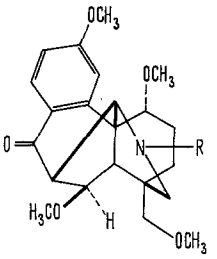
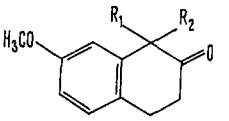


2 R = –C(=O)–H
3 R = H
4 R = –C(=O)–CH$_3$
5 R$_1$ = H, R$_2$ = H



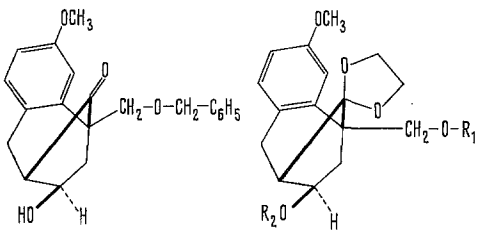
6 R$_1$ = H, R$_2$ = –CH$_2$–CH=CH$_2$
7 R$_1$ = –CH$_2$–O–CH$_2$–C$_6$H$_5$, R$_2$ = –CH$_2$–CH=CH$_2$
8 R$_1$ = –CH$_2$–O–CH$_2$–C$_6$H$_5$, R$_2$ = –CH$_2$–CH(OH)–CH$_2$(OH)
9 R$_1$ = –CH$_2$–O–CH$_2$–C$_6$H$_5$, R$_2$ = –CH$_2$–C(=O)–H

Compound **7** was subjected to a catalytic osmylation with osmic acid-sodium chlorate in THF[7]. The two diastereoisomeric diols **8** (A mp 108–109°, B mp 125–130°] were obtained in equal amounts and a practically quantitative yield. The absence of carbonyl absorption in the IR of both products indicated that they existed as the hemi-ketal tautomers. The diastereo-isomers **8** were treated with an excess of metaperiodate in aqueous THF. The aldehyde **9** [IR: 1726, 1715 cm^{-1} (–CH=O, >C=O); NMR: broad singlet (1H) $\tau = 0.49$ ppm (–CH=O)] was obtained in both cases in a quantitative yield. Compound **9** underwent a quantitative aldol condensation to the hydroxy ketone **10** by heating with a large volume of 0.03 M aqueous methanolic sodium hydroxide for 30 h at 55 °C. The hydroxy ketone **10** obtained in this manner was homogeneous in TLC and sufficiently pure for further work [IR (CCl_4): 3600, 3475 (OH), 1755 cm^{-1} (C=O); $m/e = 338$][8].

The hydroxy ketone **10** was converted to the ketal **11** (mp 95–97°; $m/e = 382$] by treatment with ethylene glycol and *p*-toluenesulfonic acid in refluxing benzene. The yield of the ketal **11** after recrystallization from ether was 88%.

The next operation which had to be executed was the transfer of the benzyl blocking group from the primary to the secondary alcoholic function, i.e. compound **11** had to be converted to its isomer **17**. While this process required a number of steps, it has to be emphasized that these were simple and nearly quantitative and thus *the overall yield was finally raised to* **83%**.

Acetylation of **11** with acetic anhydride and pyridine gave the acetoxy derivative **12** [mp 81–82°; $m/e = 424$]. Compound **12** was subjected to hydrogenolysis in ethanol with 10% palladium-charcoal. The oily product **13** was homogeneous in TLC and immediately used for further work [$m/e = 334.1426$; IR ($CHCl_3$): 3550 (OH), 1726 cm^{-1} (–OAc)]. The alcoholic function in **13** was now blocked



10

11 R$_1$ = –CH$_2$–C$_6$H$_5$, R$_2$ = H
12 R$_1$ = –CH$_2$–C$_6$H$_5$, R$_2$ = –C(=O)–CH$_3$
13 R$_1$ = H, R$_2$ = –C(=O)–CH$_3$
14 R$_1$ =  , R$_2$ = –C(=O)–CH$_3$
15 R$_1$ =  , R$_2$ = H
16 R$_1$ =  , R$_2$ = –CH$_2$–C$_6$H$_5$
17 R$_1$ = H, R$_2$ = –CH$_2$–C$_6$H$_5$

by tetrahydropyranylation with dihydropyrane in dry chloroform and a drop of hydrochloric acid. The product **14** was purified by chromatography and was homogeneous in TLC [$m/e = 418$; IR ($CHCl_3$): no OH band, 1725 cm^{-1} (–OAc)].

The acetoxy group of **14** was cleaved by reduction with lithium aluminum hydride and the oily alcohol **15** was purified by chromatography on silica gel [$m/e = 376.1882$; IR ($CHCl_3$): 3500 cm^{-1} (OH), no carbonyl absorption]. The secondary alcoholic group in **15** was now benzylated in dry dioxane with sodium hydride and benzyl chloride at reflux temperature for 18 h. Chromatography on silica gel yielded the pure oily compound **16** [$m/e = 466$; NMR: singlet (5H) $\tau = 2.64$ ppm (aromatic H of the benzyl group)].

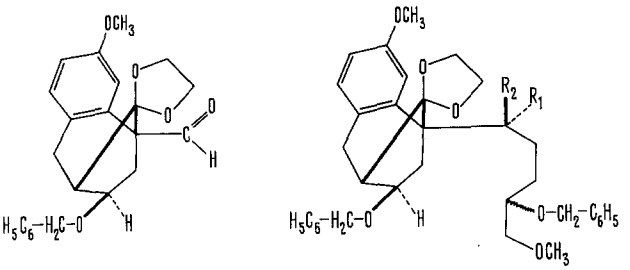
The tetrahydropyranyl group was selectively removed by treating **16** with a large volume of methanol containing 1% concentrated hydrochloric acid at room temperature for 1 h. The product **17** was purified by chromatography on silica gel and it was an oil homogeneous in TLC [$m/e = 382.1772$]. The NMR and IR spectra of **11** and **17** clearly showed the presence of an identical functional group system.

The primary alcohol **17** was oxidized by chromium trioxide in pyridine and the aldehyde **18** was obtained after chromatography on silica gel as an oil homogeneous in TLC in a yield of 85% [$m/e = 380.1623$; IR (CCl_4): 2700, 1725 cm^{-1} (HC=O); NMR: singlet (1H) $\tau = 0.17$ ppm (HC=O)].

At this point the stage was set to attach the substituted butane derivative destined to form ring A. The synthesis of this element was carried out as follows. 1-Methoxy-3-cyano-2-propene[9] (mixture of *cis* and *trans* isomers) was added to a solution of sodium in benzyl alcohol and the mixture was stirred for a week at room temperature. The crude product **19** was purified by distillation [bp 115–120°/0.3 mm Hg; yield 32%; $m/e =$ 205.1102; NMR: singlet (5H) $\tau = 2.90$ ppm (aromatic H), singlet (3H) $\tau = 6.65$ ppm (–OCH_3)]. Compound **19** was heated at reflux for 50 h with 10% sulphuric acid in methanol. The methyl ester **20** was obtained in a yield of 72% [bp 115–125°/0.1 mm Hg; $m/e = 238$; IR ($CHCl_3$): 1735 cm^{-1} (ester); NMR: singlet (5H) $\tau = 2.8$ ppm (aromatic H), two singlets (3H each) $\tau = 6.37$, 6.70 ppm (2 –OCH_3)]. Reduction of the ester **20** with lithium aluminum hydride in ether gave the alcohol **21** in a yield of 68% [bp 120–125°/0.2 mm Hg; $m/e = 210.1257$]. Finally, tosylation of **21** with tosyl chloride and pyridine followed by exchange of the tosyl group with lithium bromide in acetone gave the bromo derivative **22** in a 75% yield. The product was purified by chromatography on silica gel [$m/e = 272$, 274; high resolution $m/e =$ 272.0411; NMR: singlet (5H) $\tau = 2.67$ ppm (aromatic H), singlet (3H) $\tau = 6.65$ ppm (–OCH_3)].

One mole of the aldehyde **18** in THF was added to five moles of the Grignard reagent prepared from the bromide **22** in the same solvent. Work-up and chromatography on silica gel gave the alcohol **23**[10] [NMR: singlet (10H) $\tau = 2.68$ ppm (aromatic H of benzyls), multiplet (4H) centered at $\tau = 6.00$ ppm (dioxolane protons), two singlets (3H each) $\tau = 6.31$, 6.66 ppm (2 –OCH_3)] in a yield of 91%. This material was homogeneous in TLC and it turned out to be sterically homogeneous with respect to the R_1, R_2 asymmetric center[11].

The alcohol **23** was oxidized to the ketone **24** by the Jones' reagent in a yield of 94%. The product was homogeneous in TLC without purification [IR (CCl_4): 1700 cm^{-1} (ketone), no OH absorption]. Reduction of compound **24** with lithium aluminum hydride in dioxane at 90° – the stereochemical outcome is temperature dependent – gave a mixture (yield 97%) of the alcohols **25** and **23** in a ratio 7:3. The products were acetylated for 8 h with acetic anhydride and pyridine at room temperature. Only the desired epimer **25** acetylated under these conditions. The acetate was separated by chromatography on silica gel and the pure epimer **25** was obtained by saponification with methanolic potassium hydroxide.



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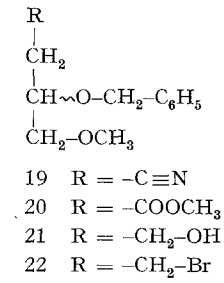


19 R = –C≡N
20 R = –$COOCH_3$
21 R = –CH_2–OH
22 R = –CH_2–Br

23 R_1 = H, R_2 = OH
24 R_1R_2 = =O
25 R_1 = OH, R_2 = H
26 R_1 = –OCH_3, R_2 = H

* Presented at a seminar at the Organic Chemistry Laboratory, ETH, Zurich, Switzerland on June 24, 1969.

[1] K. Wiesner, F. Bickelhaupt and D. R. Babin, Experientia *15*, 93 (1959); K. Wiesner, F. Bickelhaupt, D. R. Babin and M. Götz, Tetrahedron Lett. *3*, 11 (1959); Tetrahedron *9*, 254 (1960). – K. Wiesner, D. L. Simmons and R. H. Wightman, Tetrahedron Lett. *15*, 23 (1960).

[2] K. Wiesner, M. Götz, D. L. Simmons and L. R. Fowler, Coll. Czech. chem. Commun. *28*, 2462 (1963).

[3] M. D. Soffer, J. C. Cavagnol and H. E. Gellerson, J. Amer. chem. Soc. *71*, 3857 (1949).

[4] IR- and NMR-spectra were recorded for all compounds and are discussed only in specially relevant cases. All crystalline compounds gave satisfactory elemental analyses.

[5] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz and R. Terrell, J. Amer. chem. Soc. *85*, 207 (1963).

[6] C. L. Graham and F. J. McQuillin, J. chem. Soc. (*1963*), 4634.

[7] K. Wiesner, K. K. Chan and C. Demerson, Tetrahedron Lett. (*1965*), 2893.

[8] The exo configuration of the hydroxyl in **10** is supported by the NMR spectrum [quadruplet (1H) centered at $\tau = 5.70$ ppm (–CH–OH)] and by the finding that this configuration may be inverted by oxidation of the derivative **11** to the corresponding ketone, followed by borohydride reduction to the epimeric alcohol.

[9] C. F. Koelsch, J. Amer. chem. Soc. *65*, 2461 (1943).

[10] The intermediates **23** through **29** were mixtures of benzyloxy epimers due to the uncontrolled asymmetric center in the sidechain. Since they did not yield molecular ions in mass spectrometry, they were characterized exclusively by apparent homogeneity in TLC and by NMR. The last method was very reliable since it clearly showed the presence of all functional groups.

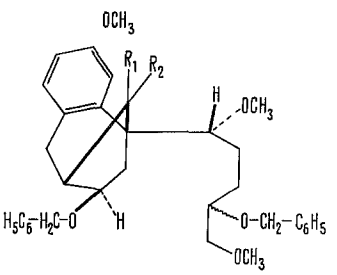
[11] When the synthesis was carried to conclusion with the asymmetric center (R_1, R_2) unchanged as in **23**, ring A methoxy epimers of compounds **2**, **3** and **4** resulted. Since the configuration of the ring A methoxyl in delphinine[1] is known from degradative data, the configuration of **23** must be as given. We believe that the stereospecificity of the Grignard reaction may be explained by the formation of a magnesium complex involving the aldehyde and one or both of the dioxolane oxygens. Such a complex would make the free rotation of the aldehyde group impossible and an attack of the Grignard reagent from the less hindered side would lead to **23**.

The recovered epimer **23** was added to the next oxidation run.

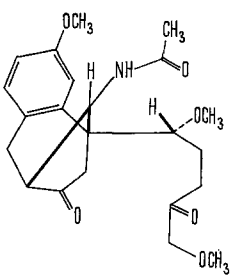
The alcohol **25** was methylated in refluxing dioxane with sodium hydride and an excess of methyl iodide for 5 h. The methyl ether **26** was obtained in a yield of 95% after chromatography on silica gel [NMR: singlet (10H) $\tau = 2.68$ ppm (aromatic H of the benzyl groups), singlets (3H each) $\tau = 6.27$, 6.59, 6.62 ppm (3 $-OCH_3$)][12].

The ketal **26** was heated under reflux in 75% aqueous acetic acid for 18 h. The TLC homogeneous ketone **27** [IR (CCl_4): 1755 cm^{-1} (ketone)] was obtained in a quantitative yield. Compound **27** was now subjected to amination with Raney nickel in methanolic ammonia exactly as worked out in our model experiments[13]. However, in the present case the desired *anti* isomer **28** was obtained stereoselectively [ratio *anti*:*syn* = 10:1, overall yield 97%].

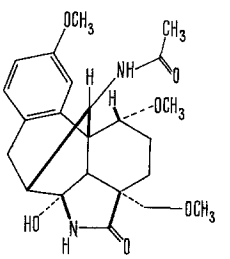
The crude amine **28** was acetylated with acetic anhydride-pyridine, the benzyl groups removed by hydrogenolysis and the two liberated alcoholic functions oxidized by chromium trioxide in pyridine. The diketone **29** was separated by chromatography on silica gel from the small amount (5%) of the undesired *syn* epimer and purified by crystallization from methanol. The overall yield of



27 $R_1R_2 = =O$
28 $R_1 = H$, $R_2 = -NH_2$



29



30

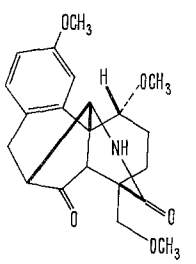
pure **29** from the crude amine **28** was 50% [mp 100–102°; IR (KBr): 1745, 1720 cm^{-1} (ketones), 1660 cm^{-1} (amide); NMR: singlets (3H each) $\tau = 6.23$, 6.52, 6.57 ppm (3 $-OCH_3$), singlet (2H) $\tau = 5.93$ ppm ($-\overset{O}{\overset{\|}{C}}-CH_2-O-$); $m/e = 403$].

The diketone **29** was heated for 6 h with 5 moles of potassium cyanide[8] in aqueous ethanol under reflux. The lactamol **30** resulted stereospecifically in a yield of 91% [mp 235–238° (chloroform-ether); IR (KBr): 1720, 1665 cm^{-1} (amides); NMR: singlets (3H each) $\tau = 6.18$, 6.58, 6.66 ppm (3 $-OCH_3$), 8.08 ppm ($-\overset{O}{\overset{\|}{C}}-CH_3$)].

The lactamol **30** was now converted to the keto lactam **31** in an overall yield of 64% by reflux in methanol-concentrated hydrochloric acid (1:1) for 3×24 h. After each reflux period the product was separated by crystallization and the mother liquors were treated again [mp 266–268° (methanol); IR (KBr): 1740 (ketone), 1670 cm^{-1} (lactam); NMR: singlets (3H each) $\tau = 6.20$, 6.57, 6.63 ppm (3 $-OCH_3$); $m/e = 371$].

The keto lactam **31** was reduced with lithium aluminum hydride in refluxing dioxane. The mixture of the amino alcohols **32** and **33** was separated by chromatography on alumina. The ratio of the two products was 1:1 and the yield was 76%. The desired epimer **32** was recrystallized from methanol [mp 226–228°; $m/e = 359$]. The oily epimer **33** was converted to the ketone **34** [IR (CCl_4): 1740 cm^{-1}] by Jones' oxidation in a quantitative yield. The ketone **34** was subjected without purification to a reduction with sodium in boiling absolute ethanol. The alcohols **32** and **33** were again obtained (yield 74%, ratio 7:3) and separated by chromatography.

The hydroxy amine **32** was methylated with sodium hydride and methyl iodide in refluxing dioxane for 3 h. The oily product **35** was purified by chromatography on silica gel [yield 96%; NMR: singlets (3H each) $\tau = 6.23$, 6.68, 6.73, 6.77 (4 $-OCH_3$), 7.73 ppm ($N-CH_3$); $m/e = 387$]. Compound **35** was oxidized with an excess of potassium permanganate in acetone-acetic acid (20:1) at room temperature for 24 h. The crude formyl derivative **36** was purified by chromatography on silica gel (yield 95%) and crystallization from ether [mp 158–160°; NMR: singlet (1H) $\tau = 2.17$ ppm ($N-CH{=}O$); IR (CCl_4): 1662 cm^{-1} ($N-CH{=}O$); $m/e = 401$]. Jones' oxidation of compound **36** gave the synthetic racemic compound **2** in a yield of 67%. The oily product was purified on silica gel plates



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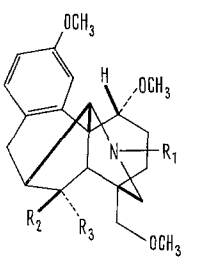

32 $R_1 = H$, $R_2 = OH$, $R_3 = H$
33 $R_1 = H$, $R_2 = H$, $R_3 = OH$
34 $R_1 = H$, $R_2R_3 = =O$
35 $R_1 = -CH_3$, $R_2 = -OCH_3$, $R_3 = H$
36 $R_1 = -C(=O)H$, $R_2 = -OCH_3$, $R_3 = H$

[12] Compound **26** is significantly different in the NMR from the methylation product of the alcohol 23 [singlets (3H each) $\tau = 6.29$, 6.47, 6.67 ppm]. The two compounds differ also very strongly by their chromatographic behaviour. Consequently, the stereochemical purity of **26** is assured.

[13] K. WIESNER and J. ŠANTROCH, Tetrahedron Lett. (*1966*), 5939. – K. WIESNER, WEN-LING KAO and J. ŠANTROCH, Can. J. Chem. *47*, 2431 (1969).

[14] A direct conversion of **35** to **2** was also achieved by an excess of potassium permanganate in acetone-acetic acid (5 days; yield 82%).

until TLC homogeneous. Over 500 mg of the pure material were synthesized [IR (CCl_4): 1690, 1655, 1600 cm^{-1}; NMR: singlet (1H) $\tau = 1.93$ ppm (N–CH=O), singlets (3H each) $\tau = 6.12$, 6.72, 6.74, 6.77 ppm (4 $-OCH_3$); $m/e = 415$][14]. The synthetic compound **2** was hydrolyzed by heating with methanol-concentrated hydrochloric acid (9:1) at reflux for 24 h. The product **3** was purified by chromatography and crystallization from ether [yield 94%; mp 176°; $m/e = 387$].

Finally, acetylation of the synthetic secondary amine **3** with acetic anhydride-pyridine gave compound **4** in a yield of 95% [mp 188–190° (hexane-ether); IR (CCl_4): 1685, 1650, 1600 cm^{-1}; NMR: singlet (3H) $\tau = 7.90$ ppm ($-\overset{\overset{O}{\|}}{C}-CH_3$); $m/e = 429$].

The totally synthetic racemates **2**, **3** and **4** were proved to be identical with the corresponding optically active 'natural' compounds[2] by TLC in several systems, IR in chloroform and carbon tetrachloride, NMR and mass spectroscopy. Work on the construction of the C–D ring system of delphinine is in progress[15].

Zusammenfassung. Die stereoselektive Totalsynthese eines Delphininabbauproduktes wird beschrieben. Dieses Produkt, das 5 Ringe und 5 Substituenten besitzt, ist von Delphinin aus leicht zugänglich und kann deshalb als Relais-Verbindung für die Totalsynthese dieses Alkaloids dienen.

K. Wiesner, E. W. K. Jay, C. Demerson, T. Kanno, J. Křepinský, Lizzie Poon, T. Y. R. Tsai, A. Vilím and C. S. Wu

Natural Products Research Center, University of New Brunswick, Fredericton (New Brunswick, Canada), 20 April 1970.

[15] We wish to thank the National Research Council in Ottawa and the Hoffmann-La Roche Company, Nutley, New Jersey for financial support. We also thank the Merck Co., Mannheim, for a donation of a large amount of crystalline aconitine and S. B. Penick & Company, Orange, New Jersey, for a gift of a large amount of *Delphinium* seeds.

Chromosomes and Some Issues of the Evolution of the Ground Squirrel Genus *Citellus* (Rodentia: Sciuridae)

Chromosome analysis, combined with other methods of systematic zoology, paleontology and zoogeography, can be used to give an integrated analysis of the evolution of taxonomically discrete faunal elements. Such analyses are of special value in studies of the evolution, in relation to space and time, of allied Eurasian and North American forms.

The evolution of the chromosome complements of Nearctic *Citellini* has been thoroughly studied by Nadler et al.[1–10]. The understanding of the evolution of the entire Holarctic genera, however, requires inclusion of the Palearctic species. The present study concerns the chromosomes of 6 species and 20 subspecies and forms of the genus *Citellus*, and a discussion of the results in conjunction with those of Nadler. In the course of the study, we have produced a hypothetical reconstruction of the evolution of the karyotypes of the species studied, with particular reference to the correlation of the range of species with similar and differing chromosome complements.

Materials and methods. The karyotypes of the following forms of *Citellus* have been studied. *C.* (*s. str.*) *relictus relictus* Kaschk., Western Tien Shan, Kuraminsky ridge near Kamtchik pass, 2300 m above sea level, 3 ♂♂, 9 ♀♀. *C. relictus ralli* Kuznetsov, Central Tien Shan, Issyk Kul basin, Tersky Ala Tau ridge, south of the town Prjevalsk, 2100 m, 2 ♂♂. *C. dauricus dauricus* Brandt, Transbaikalia, Chita region, environs of the village Borzia, 6 ♂♂, 5 ♀♀. *C. pygmaeus pallidus* Orlov, Kalmyk A.S.S.R., State farm 'Polinniy', 3 ♂♂, 3 ♀♀. *C. p. pygmaeus* Pall., between Volga and Ural rivers, left bank of Volga, north of Astrakhan, 1 ♂, 2 ♀♀. *C.* (*Colobotis*) *fulvus oxianus* Thom., Central Kyzyl Kum desert, Bukhara region, environs of the village Mubarek, 2 ♂♂. *C. f. orlovi* Ogn., between Volga and Ural rivers, near station Dassang, 2 ♂♂, 1 ♀. *C. f. nigrimontanus* Antipin: Muyun Kum desert, Djambul region, environs of the villages Ak-kol and Oik 1 ♂, 2 ♀♀; plain at the foot of the mountains, north of Transilijski Ala Tau, 74 km west from Alma Ata, 2 ♂♂, 1 ♀; near Alma Ata 1 ♂, 1 ♀. *C. erythrogenys erythrogenys* Brandt: right bank of Ob, Novosibirsk region, environs of the village Toguchin, 2 ♂♂, 2 ♀♀; between Ob and Irtish, between the town Barnaul and the village Kalmanka, 1 ♂; s.w. Altai mountains, right bank of Irtish, environs of the village Predgornoje, 1 ♂, 1 ♀. *C. er. brevicauda* Brandt: Ala-Kul basin, near Uch-Aral, 4 ♂♂, near Ajaguz 1 ♂. *C. er. carruthersi* Thom.: Zaissan basin, Buran 3 ♂♂, 3 ♀♀; near Kokpekty, 5 ♂♂, 5 ♀♀. *C. undulatus stramineus* Obolensky, S. w. Dzungarian Ala Tau, upper course of Karoy, 2400 m, 4 ♂♂, 2 ♀♀. *C. u. eversmanni* Brandt, Altai mountains, Tchujsky highway, 1400 m, 1 ♂, 1 ♀. *C. u. undulatus* Pall., South Transbaikalia, Sayan mountains, Tunkinsky basin, right bank of Irkut, 1 ♂, 1 ♀.

Subspecific distinctions of *Citellus* are given according to Gromov[11] and Vassiljeva[12].

We have caught most of the ground squirrels in the field during the Middle Asian and Siberian expeditions throughout 1965–1968. The cytological preparations were made by the standard methods, mainly from bone marrow cells and more rarely from spleen and corneal epithelial cells. The preparation procedure included colchinization, placement in a hypotonic solution of

[1] C. F. Nadler and D. A. Sutton, Proc. Soc. exp. Biol. Med. *110*, 36 (1962).
[2] C. F. Nadler, Proc. Soc. exp. Biol. Med. *110*, 785 (1962).
[3] C. F. Nadler, Proc. XVI Intern. Congr. Zool., Washington *4*, 111 (1963).
[4] C. F. Nadler, Am. Midl. Nat. *72*, 2, 298 (1963).
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