in place of the 4-CH_2 group of glutamine and is thus a potential antagonist of this amino acid. However, there is also a structural resemblance to the lower homolog asparagine, and several *N'*-(substituted)ureidoalanine derivatives were synthesized for study in microbial and tissue culture systems.

Experimental Section[3]

L-2-*p*-Toluenesulfonamido-3-[*N'*-(substituted)ureido]propionic Acids (Table I).—All of these derivatives were prepd in a similar fashion by conversion of N^2-*p*-tolylsulfonyl-L-asparagine[4] to 3-amino-2-*p*-toluenesulfonamido-L-propionic acid by the method of Rudinger, *et al.*,[5] and finally condensation with the appropriate isocyanate. A soln of 0.009 mole of the isocyanate in 20 ml of $CHCl_3$ was added with stirring over a 2-hr period to 0.009 mole of 3-amino-2-*p*-toluenesulfonamido-L-propionic acid in 15 ml of 1 *N* NaOH, and the reaction mixt was allowed to stir an additional 16 hr at room temp. The aq phase was sepd, taken to pH 1 with HCl, and satd with NaCl. After refrigeration, the solid which formed was filtered, washed with cold H_2O, air-dried, and crystd from the solvent indicated in Table I.

TABLE I

$RNHCONHCH_2CHCO_2H$
$|$
NH
$|$
$SO_2C_6H_4$-*p*-CH_3

R group	Mp, °C	Yield, %	Empirical formula[a]
Et	180–181[b]	47	$C_{13}H_{19}N_3O_5S$
n-Pr	142–143[c]	25	$C_{14}H_{21}N_3O_5S$
n-Bu	130–131[d]	42	$C_{15}H_{23}N_3O_5S$
Allyl	141–142[d]	76	$C_{14}H_{19}N_3O_5S$
Cyclohexyl	143–144[d]	67	$C_{17}H_{25}N_3O_5S$
Ph	177–178[d]	90	$C_{17}H_{19}N_3O_5S$
2-ClC_6H_4	183–184[b]	75	$C_{17}H_{18}ClN_3O_5S$
3-ClC_6H_4	189–190[c]	75	$C_{17}H_{18}ClN_3O_5S$
4-ClC_6H_4	199–200[c]	94	$C_{17}H_{18}ClN_3O_5S$
3,4-$Cl_2C_6H_3$	211–212[b]	69	$C_{17}H_{17}Cl_2N_3O_5S$
2,5-$Cl_2C_6H_3$	189–190[c]	64	$C_{17}H_{17}Cl_2N_3O_5S$
Naphthyl	191–192[b]	66	$C_{21}H_{21}N_3O_5S$

[a] For analyses indicated by symbols, the analytical results were within ±0.4% of the calcd values. All compds were analyzed for C, H, N. [b] From 95% EtOH. [c] From EtOAc. [d] From EtOAc–hexane.

L-2-Amino-3-[*N'*-(substituted)ureido]propionic Acids (Table II).—Using comparable synthetic procedures for each compd,[6] 0.002 mole of the toluenesulfonamido derivatives previously described were dissolved in 30 ml of liquid NH_3, and approximately 0.3 g of Na was added in small pieces with stirring. The addition of Na was regulated by the disappearance of the blue color, and the reaction was considered complete when the blue color persisted for about 3 min. The excess Na was decompd by the addition of NH_4OAc, and NH_3 was allowed to evap at room temp. The residue was dissolved in a few milliliters of H_2O, acidified to pH 3 with dil HCl, and placed in a refrigerator. The crystals which formed were recrystd from EtOH–H_2O and dried over $CaCl_2$ *in vacuo*.

TABLE II

$RNHCONHCH_2CHCO_2H$
$|$
NH_2

R group[a]	Mp, °C	Yield, %	Empirical formula[b]
n-Bu	238–239	41	$C_8H_{17}N_3O_3$
Allyl	232–233	18	$C_7H_{13}N_3O_3$
Cyclohexyl hydrate	203–204	29	$C_{10}H_{21}N_3O_4$
Ph	222–223	45	$C_{10}H_{13}N_3O_3$

[a] Na–liquid NH_3 cleavage of the protective *p*-toluenesulfonamido group also hydrogenolyzed the Cl substituents on the benzene ring. [b] See Table I, footnote *a*.

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Conversion of Ergosterol into the Estrogen Neoergosterol by Direct Peroxide Cleavage

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Ergosterol and its irradiation product (vitamin D) have been shown to have marked estrogenic activity.[2] Neoergosterol was reported to demonstrate still greater estrogenic activity by the same workers.[2] Neoergosterol has been prepared by the irradiation of ergosterol in the presence of a sensitizing dye followed by a pyrolytic reaction.[3] We have now shown that by application of a new type of peroxide-induced C–C cleavage reaction,[4] neoergosterol can be prepared in a simple one-step reaction from ergosterol.

Experimental Section

Neoergosterol.—Ergosterol (1.50 g) and an equimolar amt of di-*tert*-butyl peroxide (0.550 g) were dissolved in 15 ml of H_2SO_4-washed and redistd decane. The soln was refluxed for 1 hr (174°). Crystals pptd on standing overnight and were found to be unreacted ergosterol (8%). The filtered reaction mixt was concd to a thick syrup under reduced pressure. The product was chromatographed over silica gel employing the following solvents in the order listed: hexane; 95:5 hexane–PhH; 50:50 hexane–PhH; PhH; Et_2O; and EtOH. The Et_2O eluate crystd and was recrystd twice from 95% EtOH to give (14%) neoergosterol: mp 150–151°, $[\alpha]^{25}D$ −12.1° (*c* 0.33, $CHCl_3$); lit.[5] mp 151–152°, $[\alpha]^{25}D$ −12° ($CHCl_3$). Ir and uv spectra were as expected.

(3) Melting points were determined on a Thomas-Hoover apparatus; microanalyses were carried out by Mrs. Delaney Blocker, Chemistry Department, North Texas State University, Denton, Texas.

(4) M. Zaoral and J. Rudinger, *Collect. Czech. Chem. Commun.*, **24**, 1993 (1959).

(5) J. Rudinger, K. Poduška, and M. Zaoral, *ibid.*, **25**, 2022 (1960).

(6) J. Rudinger, *ibid.*, **19**, 375 (1954).

(1) A field station of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) J. W. Cook, E. C. Dodds, C. L. Hewett, and W. Lawson, *Proc. Roy. Soc., Ser. B.*, **114**, 272 (1934).

(3) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 104.

(4) W. H. Schuller and R. V. Lawrence, *Chem. Ind. N. Z.*, **6**, 203 (1970).

(5) H. H. Inhoffen, *Justus Liebigs Ann. Chem.*, **497**, 130 (1932).