

ENCYCLOPEDIA OF ENDOCRINOLOGY

by

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SECTION I

Classified Index of the Steroid Hormones and Related Compounds

VOLUME II

**Androstene,
Alkyl-androstanes (-enes)
up to Ethyl- Δ^4 -androstene**

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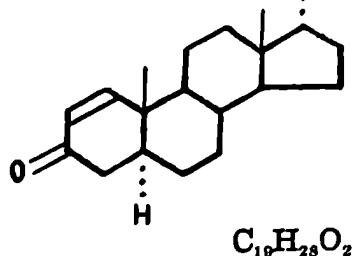
By

HANS SELYE

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Δ^1 -ANDROSTENE-3-ONE-17(α)-OL
[androstenol-(17)-one(3)]



ISOLATION:

STRUCTURE AND SYNTHESIS: (4)

M.P.:

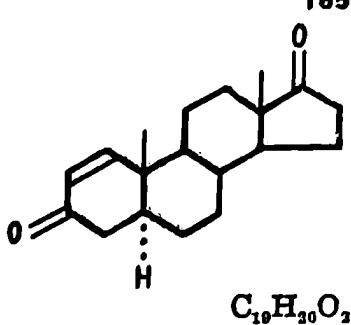
PHARMACOLOGY:

REMARKS: Cpd. previously assigned this structure [m.p. 158-9°; $[\alpha]_D^{20} = -42.3^\circ$ (alc.)], forms an ac. m.p. 118-9° and an ac.-oxime 213-5° (1,2) and as a testoid assays: 63: 100 γ /day act.-C (2); as a folliculoid: 7: 500 γ /day act.-R (2); 62: 200-250 γ /day act.-Species? (2). It is now designated as "hetero- Δ^1 -androstene-3-one-17(α)-ol" (3).

DERIVATIVES:

REFERENCES:

1. 72715
2. A18101
3. A54228
4. A38941

Δ^1 -ANDROSTENE-3,17-DIONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,3,4)**M.P.:** 138-9°: (4) $[\alpha]_D^{23} = +148.5^\circ$ (alc.): (4)

PHARMACOLOGY: Testoid: **32A**: 400 γ gives 28% increase in comb area (4); **63**: U. = 2.5 γ (4).
Folliculoid: **62**: 4 \times 100 γ inact.-M (4).

REMARKS: Cpd. previously assigned this structure [m.p. 139-40°; $[\alpha]_D^{20} = +6.8^\circ$ (alc.); dioxime m.p. 252° (1); as testoid in tests **32,33**: 4 mg. inact-C,R (1); **63**: act at 5 \times 100 γ -C (2); as folliculoid in test **62**: act. at 4 \times 100 γ -M (1)]; is now designated "hetero- Δ^1 -androstenedione" (4).

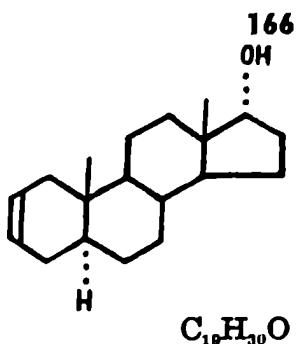
DERIVATIVES:

Dioxime 258-64°: (4)

REFERENCES:

1. 60172
2. A18101
3. A38941
4. A57429

Δ^2 -ANDROSTENE-17(α)-OL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 165°: (1)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

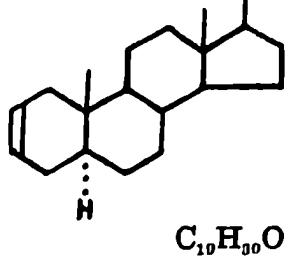
Ac. 96°: (1)

REFERENCES:

1. 70098

167
OH

Δ^2 -ANDROSTENE-17(β)-OL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

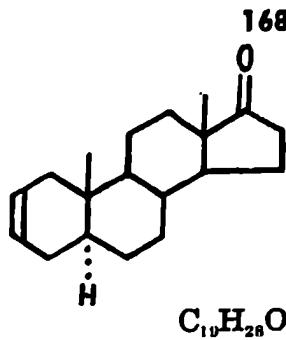
REMARKS:

DERIVATIVES:

Hexahydrobz. 117°: (1)

REFERENCES:

1. 75739

Δ^2 -ANDROSTENE-17-ONE

ISOLATION:	Ur. (♀ /c human):	(2)
	Ur. (human with ad. tumor):	(absent 4)
	Ur. (human):	(4)
	Ur. (♀ human):	(3)
	Ur. (♂ human with cancer):	(3)
	Ur. (human with Leydig cell tumor):	(5)

STRUCTURE AND SYNTHESIS: (1,2,3,5)

M.P.: 110-1°: (2)
 107-9°: (2)
 102°: (1)
 104-5°: (3)
 114-4.5°: (4)

$[\alpha]_D^{28} = +151^\circ$ (alc.): (2,3)
 $[\alpha]_D^{38} = +148^\circ$ (?): (4)

PHARMACOLOGY:

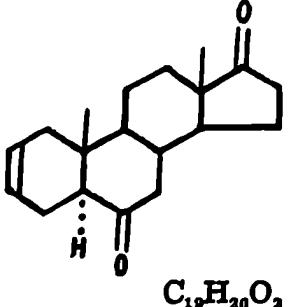
REMARKS: In ur. may be artefact. Position of double bond uncertain (2,3).

DERIVATIVES:

Semicarb. 183-95°: (2)
 Oxime 153-4°: (3,4)

REFERENCES:

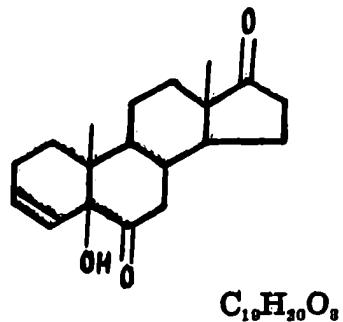
1. 70098
2. 80929
3. A37378
4. A56236
5. A57511

Δ^2 -ANDROSTENE-6,17-DIONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,2)**M.P.:** 191-1.5°: (2) $[\alpha]_D^{20} = +126^\circ$ (alc.): (2)**PHARMACOLOGY:****REMARKS:** Position of double bond uncertain (1,2).**DERIVATIVES:**

Oxide 174-6°: (2)

REFERENCES:

1. A57000
2. A50838

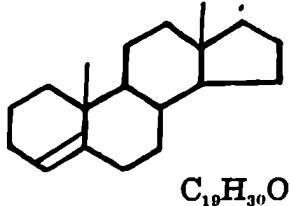
Δ^3 -ANDROSTENE-5(β)-OL-6,17-DIONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:** 238-40°: (1)**PHARMACOLOGY:**

REMARKS: 5-OH probably β (2), but listed here since cpd. was described as "androstane" derivative.

DERIVATIVES:**REFERENCES:**

1. 80945
2. 81156

**Δ^4 -ANDROSTENE-17(α)-OL
(desoxo-testosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 146-9°: (1)

PHARMACOLOGY:

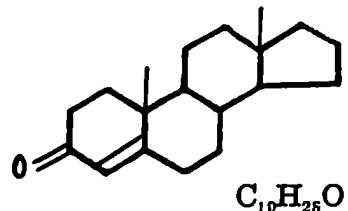
REMARKS:

DERIVATIVES:

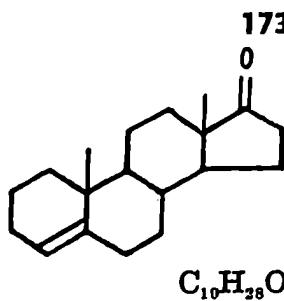
Ac. 97-100°: (1)

REFERENCES:

1. 77859

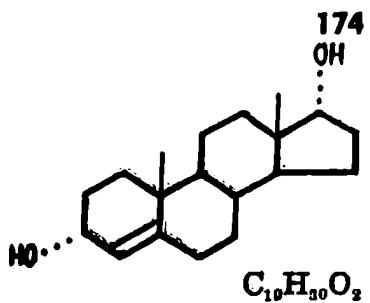
Δ^4 -ANDROSTENE-3-ONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:****PHARMACOLOGY:****REMARKS:****DERIVATIVES****17-Cl.:** (1)**REFERENCES:**

1. A54961

Δ^4 -ANDROSTENE-17-ONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:** 78-80°: (1)**PHARMACOLOGY:****REMARKS:****DERIVATIVES:****REFERENCES:**

1. 77859

Δ^4 -ANDROSTENE-3(α),17(α)-DIOL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 202-6°(u): (1)

$[\alpha]_D^{22} = +187.5^\circ$ (pyridine): (1)

PHARMACOLOGY:

Testoid: 63: U. = 0.5 γ -C (1); 32A: "epi- Δ^4 -androstendiol" as act. as " α - Δ^4 -androstendiol"-C (1).

REMARKS: Not ppt. with digitonin (1).

DERIVATIVES:

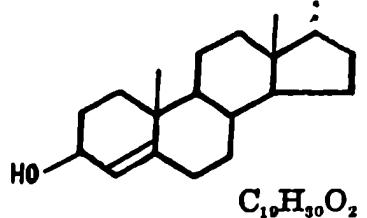
Diac. 121°(u): (1)

REFERENCES:

1. A9540

**Δ^4 -ANDROSTENE-3(β)-17(α)-DIOL
(α - Δ^4 -androstendiol)**

175



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 155.5°(u): (2)
153-4°(u): (1)

$[\alpha]_D^{19} = + 48.5^\circ$ (alc.): (1)

PHARMACOLOGY:

Testoid: **32A**: U. = 150-200 γ -C (1); **63**: U. = 1.5 γ -C (1); **32A**: up to 350 γ "4 Δ androstanediol 3,17"
inact.-C (2,3); **33**: U. = 750 γ -R (1).

Folliculoid: **7**: 2 mg./day act.-R (1); **62**: 2 mg./day act.-M (1).

REMARKS: 17-OH configuration not proven; ppt. with digitonin (2,3).

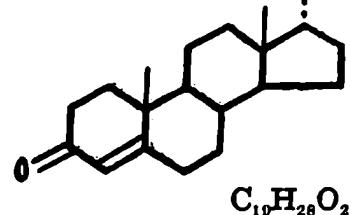
DERIVATIVES:

Diac. 101-2°(u): (1)

REFERENCES:

1. A9540
2. 55952
3. 55960

**4¹-ANDROSTENE-3-ONE-17(α)-OL
(Testosterone)**



ISOLATION: Te. (bull): (2,8,9)

STRUCTURE AND SYNTHESIS: (1,2,4,5,6,8,9,10,13,14,15,16,18,19,47,80)

Microbial Synthesis: (10,16,47,80)

M.P.: 154-5.5°: (2,4,6,9)
151°(u): (1,3,5)

$[\alpha]_D^{24} = +109^\circ$ (alc.): (2,4,6,9)
 $[\alpha]_D^{18} = +104^\circ$ (alc.): (1,5)

PHARMACOLOGY:

Testoid: **36**: I.U. = 17γ-C (45); **29**: I.U. = 13γ-C (23); **29**: I.U. = 35γ of diac., 40γ of 3-ac.-17-pr., 45γ of dipr., 200γ of 3-ac.-17-n-butyrate-C (66); **29**: I.U. = 20γ of formate, 20γ of ac., 60γ of n-butyrate, 70γ of isobutyrate, 200γ of n-valerate, 250γ of isovalerate, 350γ of caprinate, 1000γ of palmitate and 1000γ of bz.-C (65); **29**: I.U. = 25-30γ of Cl-ac., 20γ of pr., 300γ of α-br.-pr., 200γ of α-dime-amino-pr., 1 mg. of crotonate, 500γ of phenylac., 60-70γ of Cl-carb., 30-40γ of me.-carb., 100γ of et.-carb., 150γ of n-propyl-carb., 30-40γ of phenyl-carb., 150γ of benzyl-carb., 80-100γ of β-diet.-amino-et.-carb.·HCl-C (63); **29**: I.U. = 20γ of ac., 35γ of enol diac., 40γ of enol-3-pr.-17-ac., 60γ of enol-3-n-butyrate-17-ac., 150γ of enol-3-bz.-17-ac., 40γ of enol-3-ac.-17-pr., 45γ of enol-dipr., 80γ of enol-3-n-butyrate-17-pr., 60γ of 17-n-butyrate, 160γ of enol-3-ac.-17-n-butyrate; 70γ of isobutyrate, 180γ of enol-3-ac.-17-isobutyrate and enol-3-pr.-17-isobutyrate-C (103); **31**: U. = ca. 0.4γ-C (90); **63**: U. = 1-2γ-C (61,62,97); **29**: U. = ca. 10γ-C (4,22,23); **32A**: U. = 25-30γ-C (5,24); **32A**: U. = 50γ of ac.-C (79); **121**: U. = 8γ-R (78); **33**: U. = ca. 100γ-R (24); **33**: U. = ca. 25γ of ac.-R (79); **32A**: U. = 125γ of enoldiac.—act. prolonged-C (12,49); **29**: 1 mg. of urethane and n-propylurethane inact.-C (63); **80**: U. = 100γ-M (97); **45**: several esters especially me.-n-propyl-phenyl and benzyl-carbonates as act. or more act. than pr.; n-propylurethane and urethane practically inact.-R (63); **43**: at 2 mg. dose act. of Cl-, phenyl-, me., et., benzyl-, and n-propyl-carbonates increase in this order — the latter two as act. or more act. than pr.; act. of α-dime.-amino-pr., Cl-ac., α-br-pr., crotonate, phenyl-ac., increases in this order — the last as act. as pr.-R (63); **32A,33**: R.U./C.U. = 3/1-C, R (24); **45**: free cpd.: s.ves. 200%/50γ, 340%/100γ, 790%/200γ; pta. 53%/50γ, 100%/100γ, 330%/200γ; formate: s.ves. 1430%/50γ, 1900%/100γ; pta. 425%/50γ, 575%/100γ; ac.: s. ves. 1450%/50γ, 2170%/100γ; pta. 460%/50γ, 600%/100γ; pr.: s.ves. 1500%/50γ, 2300%/100γ; pta. 530%/50γ, 600%/100γ; n-butyrate: s.ves. 1200%/50γ, 1500%/100γ; pta. 100%/50γ, 575%/100γ; iso-butyrate: s.ves. 360%/50γ; pta. 120%/50γ; n-valerate: s.ves. 770%/50γ; pta. 250%/50; iso-valerate: s.ves. 143%/50γ; pta. 28%/50γ; caprinate: 50γ inact. on s.ves. and pta.; palmitate: s.ves. 57%/500γ, inact. on pta.; stearate: s.ves. 36%/500γ, inact. on pta.; bz.: s.ves. 21%/50γ, 237%/100γ; pta. inact. at 50γ, 49%/100γ; diac.: s.ves. 540%/50γ; pta. 180%/50γ-R (11,65); **131**: 6 mg./day of pr.: s.ves. 475%; pta. 470%-G (87); **37A**: free cpd.: s.ves. 43%/60γ, 290%/200γ, 570%/400γ, 1100%/600γ; pta. 57%/60γ, 190%/200γ, 360%/400γ, 715%/600γ-R (45); **138B**: 0.5 mg./day act.-R (73); **41**: oxime ca. 3 × less act. than free cpd.-C (55); **29**: enol-diac. < act. than monoac.-C (20); **43**: 2 mg. of enol-diac. more act. than monoac. on s.ves., also act. more prolonged-R (20); **85**: 500γ/day of pr. masculinizes ♀ embryo-R (34); **81**: 0.02-2.0 mg. of pr. masculinizes ♀ chicks (50); **69**: parentally ca. 25 mg. of pr. 2 × weekly act. — free cpd. < act.-Human (82,83,84,85); **128B**: prep. gl. 219 (± 18)%/1 mg., 338(± 43)%/2 mg. of free cpd.; 395(± 36)%/1 mg. of pr.-R (91); **44**: free cpd.:

s.ves. 316%/240 γ ; pta. 71%/240 γ ; oxime: s.ves. 183%/250 γ ; pta. 66%/250 γ ; bz.: s.ves. 216%/333 γ ; pta. 60%/333 γ ; ac.: s.ves. 2000%/240 γ ; pta. 430%/240 γ ; diac.: 1555%/240 γ ; pta. 330%/240 γ ; pr.: s.ves. 2090%/250 γ ; pta. 445%/250 γ -R (94); **37A**: ac. and pr. "many \times more act. than the free hormone — pr. has a more intense and more prolonged act. than the ac.-R (98); **132**: s.ves. 130(± 14)%, pta. 167(± 30)%, prep. gl. inact./25 γ of free cpd.; s.ves. 2133(± 210)%, pta. 850(± 102)%, prep. gl. 153(± 37)%/2 mg. of free cpd.; s.ves. 3116(± 181)%, pta. 983(± 114)%, prep. gl. 195(± 38)%/2 mg. of pr.-R (101,102); **96**: at 2 mg. dose level, s. ves. 5074(± 451)%; pta. 2186(± 214)%; prep. gl. 408(± 47)%-R (102); **125**: at 2 mg. dose level, s.ves. 3765(± 405)%; pta. 1770(± 170)%; prep. gl. 356(± 17)%-R (102).

Folliculoid: **62**: 1 mg./day inact.-M (61); **7**: act.-R (68); **107B**: at 1 mg./day no vag. cornification but *metrotropic* and *mammotrophic* act.-R (54); **107A**: 2 mg./day *metrotropic* and *mammotrophic*-R (54); **17B**: 1 mg./day of pr. act. in ♀ and ♀/c R (30); **39B**: pr. causes vag. opening and is *metrotropic*-R (25,26,27,28,29,31,69); **118**: 3 mg./day of pr. act. — also transitory vag. cornification-R (35); **1**: enol diac. inact. at dose of "several mgs."-Species? (20); **62**: 1 mg./day of enol diac. inact.-M (12,49); **76**: 20 mg. as *metrotropic* as 2 γ of estrone-Rb. (48); **77**: vag. opening and slight mucifying act. with 3 \times 0.5 mg. of ac. or 1 \times 2 mg. of pr.-R (48); **73**: 1 mg./day feminizes plumage-C (48); **70**: 0.2 mg./day *mammotrophic* — no vag. cornification-R (32); **67**: act. in aqueous but not in oily sol.-G (51); **128C**: 2 mg./day stratification or mucification-R (72); **39B**: 1 mg./day of pr. elicits vag. mucification and cystic glandular hyperplasia of uterus-R (73); **133A**: *Anti-Leydig cell* act.: + + +/1 mg., + + + +/10 mg.-R (70); **142**: *Anti-castration cell* act.: + + + +/0.5 mg. of free cpd. and pr.-R (81,95); **128A**: *Anti-castration cell* act.: + + +/1-2 mg. of free cpd.; + + +/1 mg. of pr.-R (91); **128A**: *Metrotropic* act.: 559(± 70)%/1 mg., 592 (± 51)%/2 mg. of free cpd. 737(± 23)%/1 mg. of pr.-R (91); **132**: *Anti-castration cell* act.: + + +/1 mg. of pr.-R (96); **74B**: 10 mg./day of pr. act. in relieving menopausal symptoms-Human (86).

Corticoid: **53**: 0.28-5 mg./day of free cpd., ac. or pr. inact. and toxic-R (36,40); **97**: 2.5 mg./day of pr. "probably not helpful" but "not harmful"-M (39); **53**: 30 mg. of pr. slightly act.-R (69); **72**: up to 10 mg./day of pr. inact. and not toxic-Ferret (41); **47A**: up to 20 mg. of free cpd. and up to 10 mg. of pr. inact.-R (53); **119**: 0.1-1 mg./day of pr. inact.-R (93); 5 mg./day of pr. act. in Addison's disease-Woman (57).

Luteoid: **48**: I.U. = 140-200 mg. of free cpd. and 50 mg. of pr.-Rb. (59); **48**: 20 mg. moderately act.-Rb. (37); **48,54**: 10-20 mg. of pr. act.-Rb. (28,52); **27**: up to 0.8 mg. inact.-G (38); **86B**: 12 mg. of pr. moderately act.-Rb. (50); **116**: 9 mg. of pr. inhibits uterine contractions-Rb. (56); **134A,134B,134C**: inact.-M, R (74,75,76); **116**: 2 \times 4.5 mg. inact. in inhibiting uterine contractions-Rb. (100); **124**: does not maintain pregnancy-M (92).

Gonadotropic: **21**: 1 mg. act.-X (42); **138A**: 0.5-2 mg./day act.-R (73); **126**: 1 mg./day of pr. act.-R (31); **125**: Te. 106(± 16)%/2 mg.-R (102).

Anti-folliculoid: **129**: Hyp.: -30(± 4)%/2 mg.; + 30(± 4)%/10 mg.; Ad.: + 18(± 7)%/2 mg., + 20(± 2)%/10 mg.; Te.: + 37(± 12)%/2 mg.; + 60(± 13)%/10 mg.-R (71); **120**: inhibits vag. cornification-M (92).

Renotropic: **143**: act. in intact. and hypx.-R (99).

Anesthetic: **11**: U. = 7 mg.-R (43); **127**: U. = 2 mg.-Fish (33); **127**: U. = 5 mg. of pr.-Fish (102).

REMARKS: "Photoproduct" of pr. obtained by ultraviolet irradiation due to doubling of molecule which masks α , β unsaturated ketone group (67).

DERIVATIVES:

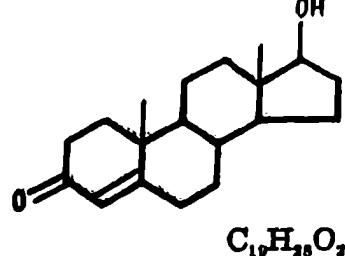
Ac.	140-2°; $[\alpha]_D^{20} = + 87.5^\circ$:	(1,4,5,6,7,9,64)
Enol-diac.	155°(u); $[\alpha]_D^{20} = - 151^\circ$ (CHCl ₃):	(12,20)
Bz.	194-6°:	(3,7,64)
Enol-bz.	183-4°:	(20)
Pr.	121-3°:	(11,63)
Enol-dipr.	127-30°:	(20)
n-butyrate	111-3°:	(11)
Isobutyrate	134-6°:	(11)

n-valerate	109-11°:	(11)
Isovalerate	138-40°:	(11)
Caprinate	55-7°:	(11)
Palmitate	72-4°:	(11)
Stearate	79-80°:	(11)
Succinate	184° and 192°:	(11,84)
α-Br.-pr.	187-8°:	(63)
α-dime.-amino-pr.	83-5°:	(63)
Crotonate	158-9°:	(63)
Phenylac.	129-31°:	(63)
3-enol-et.-ether	118-22°:	(88)
3-enol-et.-ether-17-bz.	181-92°; $[\alpha]_D = -67.5^\circ$ (pyridine) :	(89)
3-enol-et.-ether-17-pr.	143-50°; $[\alpha]_D = -140^\circ$ (CHCl_3) :	(89)
Formate	127-9°:	(64)
6-Br.-bz.	176-7°:	(46)
Oxime	222-3°:	(1,4,5,6,7,9,11)
Semicarb.	225°:	(19)
3-enol-ac.-17-pr.	140-1°:	(103)
3-enol-ac.-17-n-butyrate	96.5-8°:	(103)
3-enol-ac.-17-isobutyrate	134-6°:	(103)
3-enol-pr.-17-ac.	139.5-41°:	(103)
3-enol-bz.-17-ac.	192-3°:	(103)
3-enol-pr.-17-isobutyrate	133.5-5°:	(103)
3-enol-n-butyrate-17-ac.	97-9°:	(103)
3-enol-n-butyrate-17-pr.	79-80°:	(103)
Tetraacetyl-glucoside	165-6°; $[\alpha]_D^{18} = +49.5^\circ$ (CHCl_3) :	(21)
Glucoside	213-4°:	(21)
"Photoproduct" of pr.	350-5°; $[\alpha]_D^{22} = +47.3^\circ$ (CHCl_3) :	(67)
Cl.-carb.	139-40.5°:	(63)
Me.-carb.	140.5-1.5°:	(63)
Et.-carb.	141-2°:	(63)
Phenyl-carb.	144.5-5.5°:	(63)
n-propyl-carb.	87-9°:	• (63)
Benzyl-carb.	156.5-7.5°:	(63)
β-diet.-amino-et-carb. · HCl (+½ H_2O)	178-80°:	(63)
Urethane (+½ H_2O)	155-7°:	(63)
n-propylurethane	190-1°:	(63)
Cl.-ac.	133-4°:	(63)
n-butyrate-carb.	oil:	(63)

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| 3. 54131 | 24. 55960 | 45. 56092 | 66. 70024 | 87. A38456 |
| 4. 32108 | 25. A30158 | 46. 67266 | 67. A57497 | 88. A58075 |
| 5. 55050 | 26. A10993 | 47. 75057 | 68. 55958 | 89. 72178 |
| 6. 50272 | 27. A18420 | 48. 69323 | 69. A2410 | 90. 71314 |
| 7. 59165 | 28. 71505 | 49. 71858 | 70. A38086 | 91. A56752 |
| 8. 32863 | 29. A31983 | 50. 71207 | 71. A37637 | 92. A36553 |
| 9. 32864 | 30. A19002 | 51. A15263 | 72. A37486 | 93. A38216 |
| 10. A22296 | 31. 75107 | 52. A16346 | 73. 69957 | 94. A15289 |
| 11. 64021 | 32. 66259 | 53. A31765 | 74. 71549 | 95. A320 |
| 12. 66866 | 33. A38070 | 54. 69956 | 75. 35972 | 96. A37513 |
| 13. A10455 | 34. 72085 | 55. A30100 | 76. 76422 | 97. 63734 |
| 14. 77850 | 35. A31650 | 56. A2959 | 77. A19457 | 98. 66926 |
| 15. 71857 | 36. 75963 | 57. A15739 | 78. 38025 | 99. A35219 |
| 16. 69403 | 37. 67357 | 58. A38251 | 79. 66864 | 100. A30475 |
| 17. A16345 | 38. A7923 | 59. A50335 | 80. 75101 | 101. A38071 |
| 18. 79003 | 39. A35567 | 60. A38475 | 81. 70000 | 102. 100000 |
| 19. 80067 | 40. 76576 | 61. 75055 | 82. 76971 | 103. 75749 |
| 20. 67263 | 41. A18259 | 62. A2569 | 83. 76970 | |
| 21. A32200 | 42. 75731 | 63. 70023 | 84. A32482 | |

**Δ^4 -ANDROSTENE-3-ONE-17(β)-OL
(cis-testosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 220-1°: (1)

$[\alpha]_D^{22} = +71.5^\circ$ (alc.): (1)

PHARMACOLOGY:

Testoid: 29: LU. = ca. 400 γ of free cpd., 450-500 γ of ac. and 750 γ of bz.-C (1,2); 45: 1 mg./day inact. on s.ves. and pta.-R (1); 128B: prep. gl. + 114(± 39)% /2 mg.-R (3).

Folliculoid: 128A: no *metrotropic* act. at 2 mg.; *Anti-castration* cell act. 0 - +/2 mg.-R (3).

Luteoid: 46: 50 mg. of free cpd.; pr. or ac. slight act. if any-Rb. (4).

Anti-folliculoid: 129: up to 10 mg. slight act. if any; 1 mg. of pr. or ac. inact.-R (4).

Anesthetic: 11: U. = 10 mg. of free cpd.; 15 mg. of ac., and 20 mg. of pr. inact.-R (4); 127: U. = 1.2 mg. of free cpd. and ac., 3.0 mg. of pr.-Fish (4).

REMARKS:

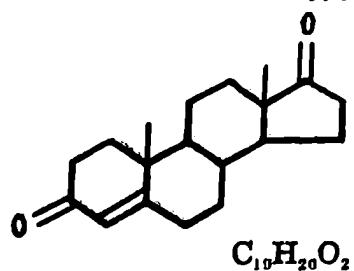
DERIVATIVES:

Ac.	115.5-6.5°: (1)
Oxime	223-5°: (1)
Bz.	136-7.5°: (1)
Semicarb.	221-2°: (1)
Pr.	92.5-3.5°: (4)

REFERENCES:

1. 59165
2. 69949
3. A56752
4. 100000

Δ⁴-ANDROSTENE-3,17-DIONE
(Androstenedione)



ISOLATION: Ad.: (60)

STRUCTURE AND SYNTHESIS: (1,3,4,5,6,7,8,10,12,13,14,39,43)

Microbial Synthesis: (10,13,43,49)

M.P.: 169°(u):	(1,8,9,10)
172-4°:	(11,14,39)
173-4°:	(3,4,5)
142-4° (labile modification):	(11)

$[\alpha]_D = + 199^\circ (\text{CHCl}_3)$:	(1)
$[\alpha]_D^{18} = + 185^\circ (\text{alc.})$:	(1)
$[\alpha]_D = + 190^\circ (\text{alc.})$:	(11)

PHARMACOLOGY:

Testoid: **29**: I.U. = 120 γ -C (18); **36**: I.U. = ca. 100 γ -C (20); **29**: I.U. = 200-300 γ of enol bz. and 150-180 γ of enol ac.-C (15); **29**: U. = ca. 100 γ -C (17,18); **32A**: U. = 200 γ -C (1,3,41); **31**: U. = ca. 0.5 γ -C (51); **33**: U. = 0.5 mg.-R (3,41); **63**: U. = 0.2-1 γ -C (8,45,50); **32A,33**: R.U./C.U. = 2-3/1-C, R (41); **45**: 200 γ /day of enol bz. inact.; enol ac.: s.ves. 150%/200 γ ; pta. 40%/200 γ -R (15); **80**: U. = 350 γ -M (8,45); **138B**: 1 mg./day act.-R (52); **37A**: s.ves. 214%/250 γ , 370%/500 γ , 730%/1000 γ ; pta. 170%/250 γ , 270%/500 γ , 1610%/1000 γ -R (20); **45**: s.ves. 25 γ inact., 107%/50 γ , 260%/100 γ , 550%/200 γ ; pta. 25 γ inact. 28%/50 γ , 120%/100 γ , 200%/200 γ -R (54); **128B**: prep. gl.: 205 (\pm 39)%/2 mg.-R (58); **44**: s.ves. 117%/250 γ ; pta. 54%/250 γ -R (22); **132**: at 2 mg. dose level: s.ves. 750(\pm 104)%; pta. 666(\pm 52)%, prep. gl. 120(\pm 19)%-R (59).

Folliculoid: **5**: 2-4 mg. inact.-M (1); **7**: 200-400 γ act.-R (1,30); **39B**: *Metrotropic* act.-R (23,28); **76**: 20 mg. as *metrotropic* as 10 γ estrone-Rb. (29); **66**: 1 mg./day *Anti-castration cell, mammatropic*, slight *metrotropic* and slight vag. mucifying act.-R (32,34); **39B**: 4 \times 2 mg. vag. mucifying-R (29); **38**: mitogenic and mucifying-R (27,28); **39B**: 4 mg./day vag. cornifying-R (23); **128C**: 4 mg./day stratifying or mucifying-R (26); **1**: 2 mg. of enolbz. and 5 mg. of enol ac. inact.-R (15); **73**: 1 mg./day feminizes plumage-C (29); **67**: act.-G (35); **133B**: *Anti-Leydig cell* act. +/10 mg.-R (53); **142**: *Anti-castration cell* act. + + + +/0.5 mg.-R (55); **128A**: *Metrotropic* act. 111(\pm 5)%/2 mg.; *Anti-castration cell* act. 0 - +/2 mg.-R (58).

Luteoid: **46**: I.U. = 140-200 mg.-Rb. (31,46); **49**: 30 mg. inact.-Rb. (1); **46**: +/50 mg.-Rb. (25); **Test?**: 10 mg. inact.-Rb. (6); **86B**: 12 mg. inact.-Rb. (44); **27**: up to 0.8 mg. inact.-G (36).

Anti-folliculoid: **120**: inhibits vag. cornification-R, M (27,33); **129**: 1 mg. inact.; Hyp.: 38(\pm 8)%/10 mg.; Ad.: 30(\pm 5)%/10 mg.; Te. 68(\pm 11)%/10 mg.-R (59).

Gonadotropic: **138A**: 1 mg./day act.-R (52); **21**: 12 mg. act.-X (38).

Anesthetic: **11**: U. = 10 mg.-R (40); **127**: U. = 1.5 mg.-Fish (47).

REMARKS: All references to pharmacological act. in which the cpd. is merely designated as "androstenedione" are listed on this page.

DERIVATIVES:

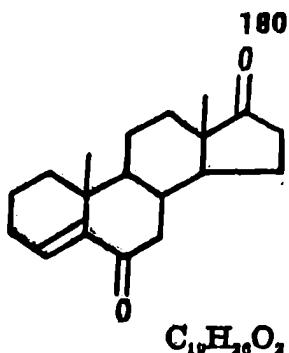
Dioxime	143°(u):	(1)
3-enol-et.-ether	152°; $[\alpha]_D^{20} = - 89^\circ$ (dioxane):	(56)
3-enol-et.-ether-diet. acetal	91-2.5°; $[\alpha]_D^{20} = + 141.6^\circ$ (dioxane):	(56)
3-enol-ac.	127-9°:	(15)

3-enol-bz.	176-80°:	(2)
Sulphonic acid	196°:	(57)
Sulphonic acid-me. ester	159-60°:	(57)
6-Br.	170-1°:	(10)
3-semicarb.	245°:	(12)
16-iso-nitroso	237-8°:	(48)

REFERENCES:

- | | | | | |
|------------|------------|------------|------------|------------|
| 1. 55958 | 13. 72921 | 25. 07357 | 37. 76576 | 49. A57195 |
| 2. 59166 | 14. 73592 | 26. A37486 | 38. 75731 | 50. A2589 |
| 3. 53443 | 15. 67263 | 27. 72400 | 39. 81695 | 51. 71314 |
| 4. 32747 | 16. 65325 | 28. A9480 | 40. A36744 | 52. 69957 |
| 5. 32748 | 17. 31735 | 29. 60323 | 41. 55960 | 53. A38086 |
| 6. 56271 | 18. 54129 | 30. 71855 | 42. 67266 | 54. 56241 |
| 7. 32864 | 19. 56272 | 31. A56335 | 43. A16454 | 55. 70000 |
| 8. A15309 | 20. 56092 | 32. 38576 | 44. A2959 | 56. A58075 |
| 9. A15413 | 21. A2409 | 33. A36553 | 45. 63734 | 57. A57430 |
| 10. A16455 | 22. A15269 | 34. 69958 | 46. A38712 | 58. A56752 |
| 11. 53760 | 23. 71505 | 35. A15263 | 47. A38070 | 59. 100000 |
| 12. 71857 | 24. 75903 | 36. A7923 | 48. A56999 | 60. 81793 |

4'-ANDROSTENE-6,17-DIONE



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 179-81°: (1)

[α]_D¹⁹ = + 96.8° (CHCl₃): (1)

PHARMACOLOGY: Testoid: 29: I.U. = ca. 250 γ -C (1).

Folliculoid: 23: 2 \times 100 γ inact.-R (1).

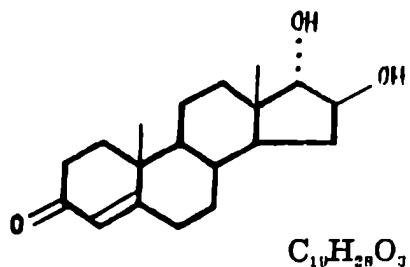
REMARKS:

DERIVATIVES:

REFERENCES:

1. 80945

**Δ^4 -ANDROSTENE-3-ONE-16(),17(α)-DIOL
(16-hydroxy-testosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 172-3°(u) : (1)

PHARMACOLOGY: **Testoid:** 63: U. = 300 γ -C (1); 33: 1 mg./day inact.-R (1).
Folliculoid: 62: 1 mg./day act.-M (1).

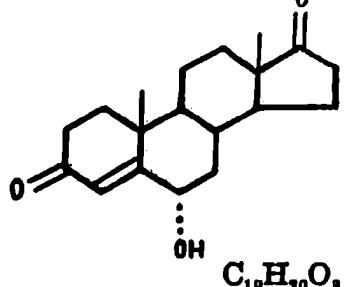
REMARKS:

DERIVATIVES:

Diac. 199°(u) : (1)
Acetonide 183-4°(u) : (1)

REFERENCES:

1. 75055

Δ^4 -ANDROSTENE-3,17-DIONE-6(α)-OL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (2)**M.P.:****PHARMACOLOGY:**

Folliculoid: 55: vag. stratification or cornification with 5 mg. of ac.-R (1,3).

Luteoid: 46: 4.5 mg. of ac. inact-Rb. (5).

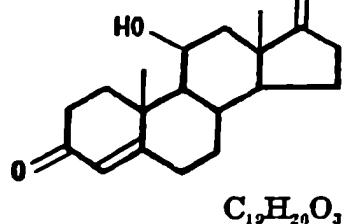
Anesthetic: 11: Act. doubtful (1,4).

REMARKS:**DERIVATIVES:**

Ac. 174-6°; $[\alpha]_D^{27} = +153.5^\circ$ (acetone): (2)

REFERENCES:

1. A36744
2. A36674
3. A37486
4. A38070
5. A58335

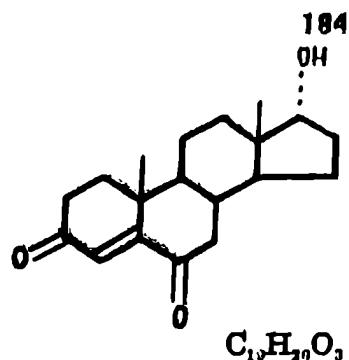
Δ^4 -ANDROSTENE-3,17-DIONE-11()-OL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)

M.P.: 190-2°: (1)

PHARMACOLOGY:**REMARKS:****REFERENCES:****REFERENCES:**

1. A9076

**Δ^4 -ANDROSTENE-3,6-DIONE-17(α)-OL
(β -keto-testosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 203-5°(u): (1)

$[\alpha]_D^{22} = -58^\circ$ (acetone): (1)

PHARMACOLOGY: Testoid: 32A: 4 mg. of ac. inact.-C (1,2); 33: 2 mg./day of ac. inact.-R (1).
Folliculoid: 62: 1 mg./day of ac. act.-M (1,2).

REMARKS:

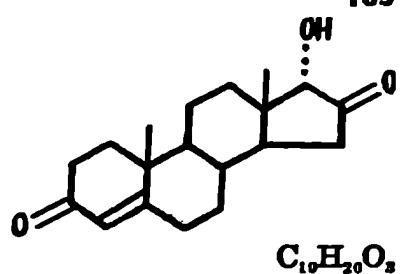
DERIVATIVES:

Ac. 198-201°(u); $[\alpha]_D^{22} = -47^\circ \pm 1.4^\circ$ (acetone): (1,2)

REFERENCES:

1. 60173
2. 55960

**Δ^4 -ANDROSTENE-3,16-DIONE-17(α)-OL
(16-keto-testosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.:

PHARMACOLOGY: Corticoid: Test?: inact.-Species? (2).

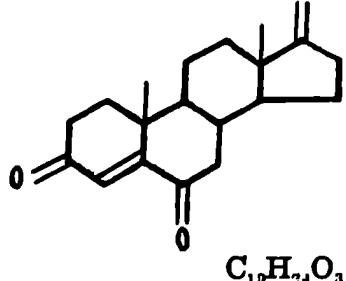
REMARKS:

DERIVATIVES:

Ac. 194-5°: (1,2)

REFERENCES:

1. A54230
2. A56999

Δ^4 -ANDROSTENE-3,6,17-TRIONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,2)

M.P.: 216-7°(u): (1)

 $[\alpha]_D^{22} = +42^\circ \pm 1.4^\circ$ (acetone): (1)

PHARMACOLOGY: Testoid: **32A**: 4 mg. inact.-C (1); **33**: 2 mg./day inact.-R (1).
Folliculoid: **62**: 1 mg./day act.-M (1).

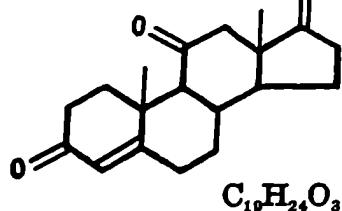
REMARKS:**DERIVATIVES:**

Trioxime 235-7°(u): (1)

REFERENCES:

1. 60173
2. A58120

Δ^4 -ANDROSTENE-3,11,17-TRIONE
(Andrenosterone; Reichstein's cpd. "G")



ISOLATION: Ad.: (2,3)

STRUCTURE AND SYNTHESIS: (1,2,3,4,5,6,7,8)

M.P.: 222-5°: (1,3)
 220-3°: (2)
 217-22°: (6)
 214-7°(u): (8)

$[\alpha]_{D}^{25} = +364^\circ$: (1)
 $[\alpha]_{D}^{20} = +262^\circ \pm 3^\circ$ (alc.): (2)

PHARMACOLOGY:

Testoid: **31**: U. = ca. 3.5γ -C (3); **41**: 1/6 to 1/4 as act. as androsterone-C (8); **106**: s.ves. 31%/
 125γ ; pta. 110%/125 γ -R (10).

Folliculoid: Test?: 10γ inact.-M (3); **67**: act.-G (9).

Corticoid: Test?: "may not possess any act."- (7).

REMARKS:

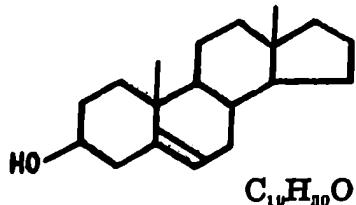
DERIVATIVES:

Disemicarb. ca. 270°: (2)

REFERENCES:

1. 72170
2. 34911
3. 63694
4. 63690
5. A9076
6. A9075
7. A33510
8. 66643
9. A15263
10. A37407

**Δ^5 -ANDROSTENE-3(β)-OL
(desoxo-dehydro-androsterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P. 131°: (5)
104°: (1)
137°: (3)

$[\alpha]_D^{20} = -48^\circ$ (alc.): (5)
 $[\alpha]_{5461} = +21.3^\circ$: (1)

PHARMACOLOGY:

Testoid: Test?: "250 \times less act. than testosterone"-C (1); **29:** U. = ca. 1 mg. of 17-amine-C (2); **45:** 0.5 mg./day of 17-amine almost inact. on s.ves. and pta.-R (2).

Folliculoid: "Estrogenic act. practically nil"-M (1).

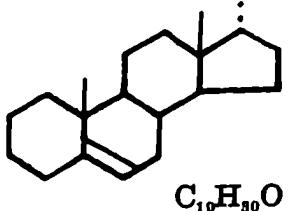
REMARKS: Ppt. with digitonin (1). Cpd. of m.p. 202° of (6) has erroneously been assigned this structure (1).

DERIVATIVES:

Ac.	114°: (1); 94°:	(3,5)
17-amine	160-2°:	(2)
17-amine.HCl	300°:	(2)
Ac.-17-Cl	160-1°; $[\alpha]_D^{20} = -56.5^\circ$ (CHCl_3): (4)	

REFERENCES:

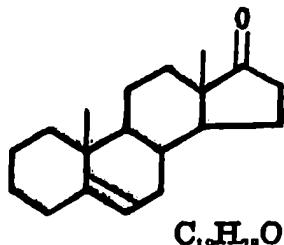
1. A18921
2. A31549
3. S0054
4. A54961
5. A50838
6. A18921

Δ^5 -ANDROSTENE-17(α)-OL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,2,3)**M.P.:** 163-5°: (1)**PHARMACOLOGY:****REMARKS:****DERIVATIVES:**

Ac. 133-5°: (1)
 3-Cl-tosylate 150°; $[\alpha]_D^{20} = -60^\circ$ ($CHCl_3$): (2)

REFERENCES:

1. 77859
2. 69135
3. A58194

Δ^5 -ANDROSTENE-17-ONE

ISOLATION: Ur. (♂ human as 3-Cl derivative): (2,6)

STRUCTURE AND SYNTHESIS: (1,2,3,4,5,6,8,10)

M.P.: 105-7°: (1)

PHARMACOLOGY: Luteoid: 46: 52 mg. of 3-Cl cpd. inact.-Rb. (9).

Anesthetic: 11: 20 mg. of 3-Cl cpd. inact.-R (7).

REMARKS: Cl-cpd. isolated from ur. is artefact (4,6); steric configuration of Cl uncertain (3,4).

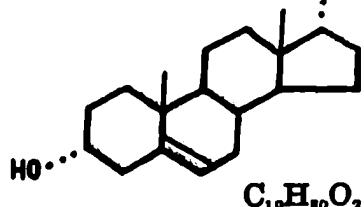
DERIVATIVES:

3-Cl	155-7°; $[\alpha]_D^{21} = +14^\circ$ (CHCl_3):	(2,4,5,10)
3-Br.	174°:	(8)
Semicarb.	285-7°:	(1)
3-Cl-oxime	169°:	(2)
3-Cl-semicarb.	275°:	(2)

REFERENCES:

1. 77859
2. 32388
3. 35029
4. 66865
5. 81144
6. 55957
7. A36744
8. A50838
9. A56335
10. A58194

Δ^5 -ANDROSTENE-3(α),17(α)-DIOL
 (Δ^5 -3-epi-oxy-17-cis-oxy-androstene; Epi-androstenediol;
 Δ^5 -3-epi-17-trans-androstenediol)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 208-9°: (1,2)

$[\alpha]_D = -56^\circ$ (alc.): (1)

PHARMACOLOGY:

Testoid: 29: I.U. = 35γ -C (1); 45: s.ves. 21%/100 γ , 80%/200 γ , 150%/500 γ , pta. 18%/100 γ , 62%/200 γ , 180%/500 γ -R (1).

Folliculoid: 107A: with 1 mg./day of "cis androstenediol" vag. cornification, *metrotropic* act. but no *mammotrophic* act.-R (3).

REMARKS:

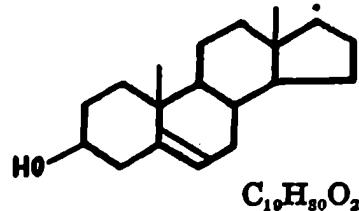
DERIVATIVES:

Diac. 155-5.5°: (1)

REFERENCES:

1. 68624
2. A33511
3. 69956

**Δ^6 -ANDROSTENE-3(β),17(α)-DIOL
(β trans-17 trans- Δ^6 -androstenediol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,3,23,24)

M.P.: 182-3°: (1,3,23,24)
178°(u): (10,22)
184-5°: (9)

$[\alpha]_D = -49.4^\circ$ (alc.): (3)
 $[\alpha]_D = -55.5^\circ$ (propanol): (10,22)

PHARMACOLOGY:

Testoid: **29:** I.U. = 500 γ -C (13); **36:** I.U. = ca. 235 γ of "transandrostenediol"-C (20); **29:** I.U. = 500 γ of diac.-C (13); **29:** U. = 350 γ -C (23); **29:** U. = 300-400 γ of diac.-C (13); **32A:** 600 γ /day inact.-C (22,37); **32A:** 600 γ /day of diac. inact.-C (22); **33:** U. = ca. 0.7 mg.-R (30); **32A:** U. = 1.3 mg.-C (10,11,30); **32A,33:** R.U./C.U. = 0.5/1-C, R (10,30); **63:** U. = 5 γ -C (28); **138B:** 1 mg./day of "androstenediol (trans)" slightly act.-R (38); **37A:** "Transandrostenediol" s.ves. 300%/500 γ , 1100%/1000 γ ; pta. 180%/500 γ , 400%/1000 γ -R (20); **45:** s.ves. inact. at 100 γ , 36%/200 γ , 115%/500 γ , 240%/1000 γ ; pta. inact. at 100 γ , 14%/200 γ , 16%/500 γ , 65%/1000 γ -R (13); **45:** diac.: s.ves. 57%/200 γ , pta. 25%/200 γ -R (13); **128B:** prep. gl. 290(\pm 33)%/2 mg.-R (41); **132:** s.ves. 117(\pm 25)%/200 γ , 150(\pm 27)%/500 γ , 125(\pm 17)%/2 mg., 167(\pm 17)%/10 mg.; pta. 178(\pm 24)%/200 γ , 256(\pm 17)%/500 γ , 222(\pm 19)%/2 mg., 267(\pm 29)%/10 mg.; prep. gl. 100(\pm 35)%/200 γ , 115(\pm 20)%/500 γ , 135(\pm 34)%/2 mg., 210(\pm 12)%/10 mg. of free cpd.; s.ves. 417(\pm 55)%; pta. 394(\pm 24)%; prep. gl. 135(\pm 8)%/2 mg. of dpr.-R (42,43); **125:** at 2 mg. dose level s.ves. 2089(\pm 162)%; pta. 1020(\pm 65)%; prep. gl. 514(\pm 102)%-R (43).

Folliculoid: **7:** 70 γ /day act.-R (10,28); **62:** 200 γ /day act.-M (10,12,28); **76:** 10 mg. of "transandrostenediol" metrotropic-Rb. (12); **107A:** no mammotropic or metrotropic act. with 1 mg./day of "transandrostenediol"-R (17); **78:** vag. opening and mucification at 2 mg./day of "transandrostenediol"-G (12); **77:** vag. stratification or cornification with 1 mg./day of "transandrostenediol"-R (12); **71:** slight metrotropic act. and vag. mucification with Δ^6 -androstenediol"-R (7,14); **73:** 1 mg./day of "transandrostenediol" feminizes plumage-C (12); **39B:** 4 mg./day of "androstenediol" metrotropic and vag. cornifying-R (16); **128C:** 0.25-4 mg./day vag. stratifying or cornifying-R (32); **130:** S/L = ca. 1-M (31); **133B:** +/10 mg. Anti-Leydig cell act.-R (39); **142:** Anti-castration cell act. +/0.5 mg. of "transandrostenediol"-R (40); **128A:** metrotropic act. 504(\pm 28)%/2 mg.; anti-castration cell act. + + - + + +/2 mg.-R (41).

Luteoid: **46:** 50 mg. of transandrostenediol inact.-Rb. (26); **46:** I.U. > 200 mg. of free cpd.; dpr. inact. at 50 mg.-Rb. (9).

Gonadotropic: **138A:** 1 mg./day of "transandrostenediol (trans)" slightly act.-R (38); **21:** up to 5 mg. of "transandrostenediol" inact.-X (29). **125:** Te. 133(\pm 36)%/2 mg.-R (43).

Anti-folliculoid: **129:** free cpd.: Hyp. 10(\pm 6)%/500 γ ; Ad. 32(\pm 4)%/500 γ ; Te. 52(\pm 3)%/500 γ ; dpr.: Hyp. 30(\pm 4)%/10 mg., Ad. 27(\pm 5)%/10 mg., Te. 44(\pm 14)%/10 mg.-R (33,43).

Anesthetic: **11:** U. > 20 mg.-R (18); **11:** U. = > 20 mg. of dpr.-R (43); **127:** U. = 1.5 mg.-Fish (35); **127:** U. = > 7 mg. of dpr.-Fish (43).

REMARKS: Cpd. shows great variability in testoid activity for reasons as yet unknown (43).

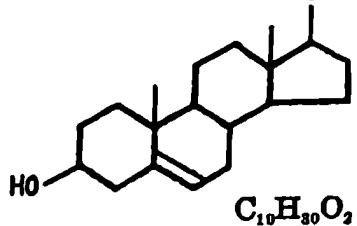
DERIVATIVES:

3-ac.	147-8°; 140°(u):	(22,24,25)
17-ac.	140.5-8.5°:	(24)
Diac.	165-0°; 159.5°(u); $[\alpha]_D^{25} = -56.5^\circ$ (alc.):	(22,24)
17-bz.	220.0-2°:	(1,2)
3-ac.-17-bz.	180-9°:	(1,2)
Dipr.	110-90°:	(9)
17-1/2 succinate	90.5-0°:	(19)
Me. ester-17-1/2 succinate	100°:	(10)
3-ac.-17-1/2 succinate	100-1.5°:	(10)
Di-p-toluolsulphonate	140-1°; $[\alpha]_D^{20} = -59^\circ$ (CHCl ₃):	(4)
Oxalic acid adduct	not formed:	(27)
Glucuronic acid	202-4°:	(36)

REFERENCES:

- | | | | | |
|-----------|------------|-----------|------------|-------------|
| 1. 59165 | 10. 55055 | 19. 82001 | 28. 71847 | 37. 53443 . |
| 2. 54131 | 11. 71555 | 20. 50002 | 29. 75731 | 38. 60957 |
| 3. 68624 | 12. 60309 | 21. 55902 | 30. 55060 | 39. A38086 |
| 4. 69135 | 13. 56341 | 22. 55956 | 31. A38863 | 40. 70000 |
| 5. 69949 | 14. A0490 | 23. 50783 | 32. A37486 | 41. A56752 |
| 6. 72400 | 15. A56752 | 24. 50272 | 33. A37637 | 42. A38071 |
| 7. A2409 | 16. 71509 | 25. 75058 | 34. A38712 | 43. 100000 |
| 8. 55720 | 17. 60056 | 26. 07357 | 35. A38070 | |
| 9. A56335 | 18. A26744 | 27. 83021 | 36. 75626 | |

**Δ^5 -ANDROSTENE-3(β),17(β)-DIOL
(3-trans-17-cis-androstendiol-■■■)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 203-4°: (6)
198-8.5°: (1)
197°: (7)
173-3.5°: (5)

PHARMACOLOGY:

Testoid: **29**: I.U. = 850-1000 γ -C (1,4); **29**: U. = ca. 350 γ -R (5); **45**: 500 γ slightly act.-R (5); **45**: 2 mg./day inact. on s.ves. and pta.-R (1); **128B**: prep. gl. 143(\pm 12)%/2 mg., 280(\pm 42)%/10 mg.-R (8); **132**: s.ves. inact, pta. 172(\pm 22)%, prep. gl. 85(\pm 16)%/2 mg. of free cpd.; s.ves. inact, pta. 172(\pm 30)%; prep. gl. 145(\pm 29)%/10 mg. of 17-pr.; s.ves. and prep. gl. inact., pta. 167 (\pm 27)%/10 mg. of diph.-R (9,10).

Luteoid: **46**: 50 mg. of free cpd., 17-pr., and 3,17-diph. inact.-Rb. (6).

Folliculoid: **128A**: metrotropic act. 67(\pm 7)%/2 mg., 19(\pm 12)%/10 mg.; anti-castration cell act. 2 mg. inact., 0 - +/10 mg.-R (8).

Anti-folliculoid: **129**: up to 10 mg. of free cpd. inact., 1 mg. of 17-pr. and diph. inact.-R (9).

Anesthetic: **11**: U. = 15 mg. of free cpd., 20 mg. of 17-pr.; diph. inact. at 20 mg.-R (9); **127**: U. = 0.8 mg. of free cpd., > 7 mg. of 17-pr.; diph. inact. at 7 mg.-Fish (9).

REMARKS: Comparatively high testoid act. of early preparation (5) probably due to contamination with 17(α) isomer (1).

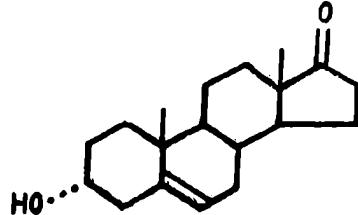
DERIVATIVES:

Bz.	150-1°:	(1)
Diac.	169.5-70.5°: (2 crystalline forms):	(1,2,3)
3-ac.-17-bz.	133-4°:	(1)
17-pr.	140°:	(6,10)
Diph.	97°:	(6)

REFERENCES:

1. 59165
2. 55958
3. 56272
4. 67949
5. 56783
6. A56335
7. 75055
8. A56752
9. 100000
10. A38071

Δ^5 -ANDROSTENE-3(α)-OL-17-ONE
 (dehydroandrosterone; epi-dehydroandrosterone; 3-epi-hydroxy-androstenone-17)



ISOLATION:

C₁₉H₃₀O₂

STRUCTURE AND SYNTHESIS: (1)

M.P.: 221°: (1)
 223°: (4)

[α]_D = 0° (alc.): (1)

PHARMACOLOGY:

Testoid: **29**: I.U. = ca. 100 γ -C (3); **45**: s.ves. inact. up to 100 γ , 29%/200 γ , 220%/500 γ ; pta. inact. up to 100 γ , 28%/200 γ , 156%/500 γ -R (3); **81**: 0.02-2 mg. of "dehydroandrosterone" masculinizes ♀-Chick (6).

Folliculoid: **81**: 0.02-2 mg. of "dehydroandrosterone" feminizes ♂-Chick (6).

Corticoid: **53**: 3 mg./day of "dehydroandrosterone" inact.-R (5).

REMARKS: Ppt. with digitonin (1).

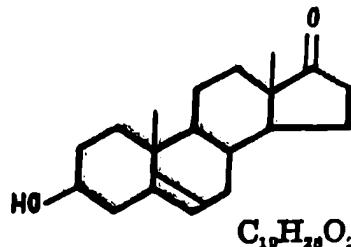
DERIVATIVES:

Me. ether	b.p. 100-10° at 0.001 mm.; [α] _D ²³ = + 111° (CHCl ₃): (2)	REFERENCES:
Oxime	204-6°: (1)	1. 67264
Ac.	173.5-4.5°: (1)	2. 66865

3. 68624
4. A33511
5. 75963
6. 71207

Δ^5 -ANDROSTENE-3(β)-OL-17-ONE

(Dehydro-iso-androsterone; dehydro-androsterone; trans-dehydro-androsterone)



ISOLATION:	Ur. (♀ human):	(40.51, absent 50)
	Ur. (bull):	(9)
	Ur. (preg. cow):	(9)
	Ur. (♂ human):	(2,3,50,52)
	Ur. (♀ human with Ad. tumor):	(24,43,45, absent 53)
	Ur. (ox):	(44)
	Ur. (preg. mare):	(58)
	Ur. (♀ /c human):	(35)
	Ur. (♂ /c human):	(54)
	Ur. (human with Cushing's syndrome):	(45)

STRUCTURE AND SYNTHESIS: (2,3,4,5,7,55,56,57)

M.P.:	148-9°:	(24,42)
	152-3°(leaflets) and 140-1°(needles):	(1)
	148°(u) (mixture of two forms):	(2,4,5)
	144-6° + 150°:	(8,57)

$$[\alpha]_D = +10.9^\circ \text{ (alc.)} : (6)$$

PHARMACOLOGY:

Testoid: **29:** I.U. = 200 γ -C (15,29); **36:** I.U. = ca. 300 γ -C (16); **29:** U. = 140 γ -C (15); **32A:** U. = 600 γ -C (1,6,37); **32A:** U. = 600-640 γ of ac. and > 1.2 mg. of bz.-C (6); **31:** U. > 2 γ -C (60); **33:** U. = 3 mg.-R (6,37); **32A,33:** R.U./C.U. = 5/1-C, R (37); **31:** 20 γ /day of glucuronide inact., 77 γ /day moderately act.-C (12); **45:** up to 500 γ inact. on s.ves. and pta.-R (15,29,39); **37A:** up to 2 mg. inact. on s.ves. and pta.-R (16); **80:** U. > 1 mg.-M (67); **121:** U. = 940 γ -R (18,19); **59:** U. = 6 γ locally, 1500 γ intramuscularly, and 2250 γ per os-C (38); **138B:** act.-R (61); **128B:** prep. gl. 271 (\pm 24)%/2 mg.-R (47); **45:** s.ves. 0%/ 500γ , 160%/ 2000γ , 300%/ 3000γ ; pta. 0%/ 500γ , 67%/ 2000γ , 135%/ 3000γ -R (69).

Folliculoid: **128C:** 2 mg./day vag. stratification or mucification, 10 mg./day vag. stratification or cornification-R (28); **7:** 1 mg. as act. as 1 γ of estrone on vag. cornification and 2 mg. as act. as 12 γ of estrone on vag. opening-R (22); **62:** 2 mg. inact.-M (6); **3:** metrotropic act. < 0.01% that of estrone-M (36); **58:** 4 mg./day of "dehydroandrosterone" vag. cornification and metrotropic act.-R (20); **7:** 2 mg./day act.-R (6,21); **76:** 20 mg. as metrotropic as 10 γ of estrone-Rb. (27); **73:** 1 mg./day feminizes plumage-C (17,27); **39A:** 1-1.5 mg./day vag. opening and cornification, metrotropic act.-R (17); **71:** vag. mucification and slight metrotropic act.-R (26); **107B:** 1 mg./day of "dehydroandrosterone" no vag. cornifying, metrotropic or mammotropic act.-R (30); **107A:** 1 mg./day of "dehydroandrosterone" persistent vag. estrus and metrotropic act. in normal and hypx.-R (30); **81:** 0.02-2 mg. of "dehydroandrosterone" feminizes ♂-Chick (32); **133B:** Anti-Leydig cell act.: +/1 mg., ++ +/10 mg.-R (62); **142:** Anti-castration cell act.: 0 - +/0.5 mg.-R (63); **128A:** metrotropic act. 160(\pm 14)%/2 mg.; anti-castration cell act.: ++/2 mg.-R (47); **77:** 1 mg./day vag. stratification-R (27).

Luteoid: **27:** up to 0.8 mg. of "dehydroandrosterone" inact.-G (46); **46:** up to 50 mg. of free cpd., ac., and 3-Cl cpd. inact.-Rb. (41,49); **48:** 40 mg. of "dehydroandrosterone" inact.-Rb. (20).

Anti-folliculoid: **129:** 2 mg. inact. on Hyp. and Ad., Te. 58(\pm 7)%/2 mg., 85(\pm 11)%/10 mg.; Hyp. 20(\pm 3)%/10 mg., Ad. 30(\pm 2)%/10 mg.-R (3).

Gonadotropic: **138A:** 1-3 mg./day act.-R (61); **122:** 2-3 mg./day act.-R (23); **21:** 10 mg. act.-X (31,33).

Anesthetic: **11:** 7 mg. of 1/2 succinate; 20 mg. of free cpd. and ac. inact.-R (34,48); **127:** U. = 1.5 mg. of free cpd. and 2 mg. of ac.-Fish (48).

REMARKS: Ppt. with digitonin (6); Oxide originally termed α later designated as β and vice versa (34,64,65,66).

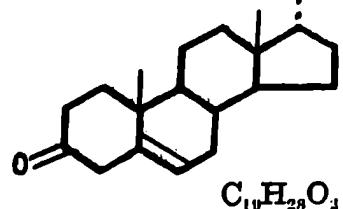
DERIVATIVES:

Ac.	171-2°:	(1,6,8)
Bz.	250°(21); $[\alpha]_D^{20} = + 26^\circ$ (CHCl_3):	(4,5,25)
Ac.-semicarb.	270°(u):	(4,5,57)
Semicarb.	273-5°:	(1,6,56)
Oxime	188-91°:	(6)
Me. ether	140-2°; $[\alpha]_D = 0^\circ$ (CHCl_3):	(10)
Tosylate	157-8°; $[\alpha]_D^{20} = - 12.1^\circ$ (dioxane):	(10,59)
Me. ester-triac. glucuronate	193-6°; $\{ [\alpha]_D = - 19.7^\circ$ (CHCl_3) : [$\alpha]_D = - 16.2^\circ$ (benzene) :	(12) (11)
β -glucoside	223-5°:	(14)
Tetraacetyl- β -glucoside	192-3.5°:	(14)
Ac.-glucuronide	194-6°(u); $[\alpha]_D^{25} = - 8.4^\circ$ (CHCl_3):	(13)
Glucuronide	262-4°(u):	(13)
Oxalic acid adduct	144°:	(42)
5:6 α -oxide	226-8.5°: (85); 229-30°: $[\alpha]_D = - 12^\circ$ (acetone):	(66) (64) { positive rotation of (65) probably misprint (64)
5:6 α -oxide-3-ac.	222-3°; $\{ [\alpha]_D^{26} = + 10^\circ$ (acetone): $[\alpha]_D^{17} = - 12^\circ$ (CHCl_3):	(65) (34,64,65)
5:6 α -oxide-3-bz.	218-20°:	(64)
5:6 β -oxide	229-30°:	(66)
5:6 β -oxide-3-ac.	$\{ 188-90^\circ$; $[\alpha]_D^{26} = + 54.4^\circ$ (acetone): 205-7°; $[\alpha]_D^{19} = - 28^\circ$ (CHCl_3):	(65) (64)
5:6 β -oxide-3-bz.	218-20°:	(64)
Ac.-p-nitrophenylhydrazone	291-2°:	(68)
$\frac{1}{2}$ succinate	257-9°:	(24)
Succinate-me. ester	155.5-6.5°:	(24)

REFERENCES:

1. 56271	15. 54129	20. 56241	43. 70088	57. 83173
2. 32388	16. 58002	30. 60956	44. 75573	58. A56072
3. A37637	17. 55720	31. 66925	45. 76322	59. A50838
4. 32747	18. 38925	32. 71207	46. A7923	60. 71314
5. 32748	19. A10771	33. 75731	47. A56752	61. 60057
6. 55957	20. 71505	34. A36744	48. A38070	62. A38086
7. 31738	21. 55058	35. 76419	49. A56335	63. 70000
8. A10372	22. A1077	36. A35039	50. A37378	64. 80045
9. 75332	23. 08772	37. 55900	51. A10775	65. 81156
10. 66865	24. 81144	38. 75101	52. A36219	66. A15412
11. 72716	25. 81156	39. 58272	53. A35703	67. 03734
12. 75026	26. A0480	40. A19775	54. A33703	68. 79074
13. 74172	27. 60323	41. 67357	55. 83085	69. 07383
14. A15412	28. A37486	42. 83021	56. A39235	

Δ^5 -ANDROSTENE-3-ONE-17(α)-OL
 $(\Delta^5$ -testosterone)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.:

PHARMACOLOGY: Testoid: **32A**: U. = 125 γ of ac.-C (1); **33**: U. = ca. 50 γ of ac.-R (1).

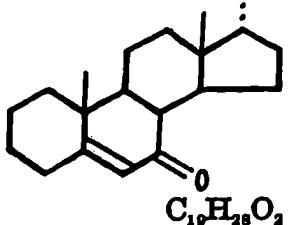
REMARKS: Free cpd. unstable (1).

DERIVATIVES:

Ac. 147°(u); $[\alpha]_{D}^{20} = -30.5^\circ$ (alc.): (1)
 Pr. 135°; $[\alpha]_D = -17^\circ$ (alc.): (2)
 Bz. 170-80°; $[\alpha]_D = +23^\circ$ (benzol): (2)

REFERENCES:

1. 66864
2. 68624

Δ^5 -ANDROSTENE-7-ONE-17(α)-OL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)

M.P.: 143-4°: (1)
141.5-2.5°: (2)

PHARMACOLOGY: Testoid: Test?: "slight act."-Species? (1).

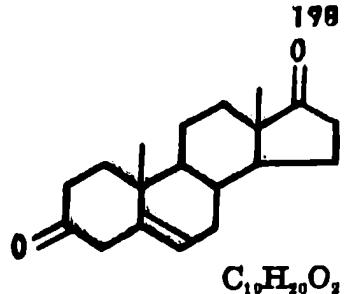
REMARKS:**DERIVATIVES:**

Ac.	{ 212-3°: (1) 215-7°: (2)
Ac.-oxime	
2:4-dinitrophenylhydrazone	
	128-31°: (1) 230-2°: (2)

REFERENCES:

1. A58104
2. 77859

Δ^5 -ANDROSTENE-3,17-DIONE



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 158°: (1)

PHARMACOLOGY: Testoid: Test?: LU. < 300 γ -C (3); **32A**: "less act. than Δ^4 -androstenedione"-C (1); Test?: "in comparison with dehydro-androsterone we find in this Δ^5 -androstenedione an increase in male and a marked decrease in female potency" (2); **33**: U. = 1500 γ -R (5).

REMARKS: Steric configuration of oxide uncertain probably (α) (1).

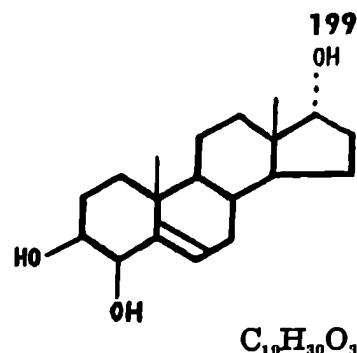
DERIVATIVES:

Dioxime 205°: (1)
5:6 oxide 265°: (4)

REFERENCES:

1. 60175
2. 71855
3. A33511
4. 67265
5. A92

Δ^5 -ANDROSTENE-3(β),4(β),17(α)-TRIOL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 258-61°: (1)
253-4°: (2)

PHARMACOLOGY:

REMARKS:

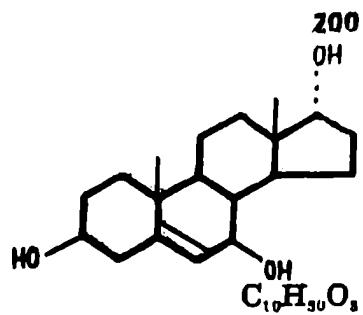
DERIVATIVES:

Diac. 155-6°: (1,2)

REFERENCES:

1. 80967
2. 69945

Δ^5 -ANDROSTENE-3(β),7(α),17(α)-TRIOL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 236°(u): (1)

$[\alpha]_D^{23} = +26^\circ$ (alc.): (1)

PHARMACOLOGY: Testoid: 63: 100 γ /day inact.-C (1).

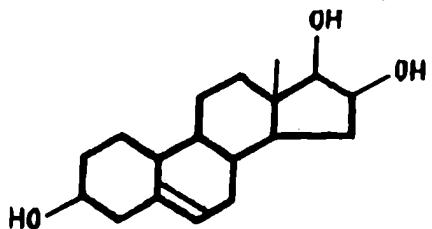
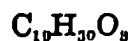
REMARKS:

DERIVATIVES:

Tribz. 250°(u); $[\alpha]_D^{23} = +87^\circ$ ($CHCl_3$): (1,2)

REFERENCES:

1. 71847
2. A18100

Δ^5 -ANDROSTENE-3(β),16(α),17(β)-TRIOL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,2)

M.P.: 273-5° (u) : (1,2)

PHARMACOLOGY: Testoid: 63: 100 γ /day inact.-C (1).

Folliculoid: 62: 1 mg./day in aqueous sol. act.-M (1).

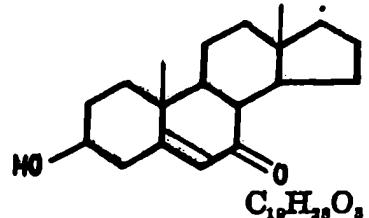
REMARKS:**DERIVATIVES:**

3-ac.	179°:	(1)
Acetonide	163-4°:	(1)
Triac.	224-6°:	(1)
3,17-diac.	204-6°:	(2)

REFERENCES:

1. 75055
2. A54229

**Δ^5 -ANDROSTENE-3(β),17(α)-DIOL-7-ONE
(7-oxo- Δ^5 -androstenediol-3,17)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 201°(u) (+H₂O): (1)

$[\alpha]_D^{20} = -133^\circ$ (alc.): (1)

PHARMACOLOGY:

Testoid: **32A**: 2 mg. of diac. inact.-C (1,3); **63**: 100 γ /day of diac. inact.-C (1); **33**: 3 mg./day of diac. inact.-R (1).

Folliculoid: **62**: 2 mg./day of diac. inact.-M (1); **7**: 2 mg./day of diac. inact.-R (1).

REMARKS:

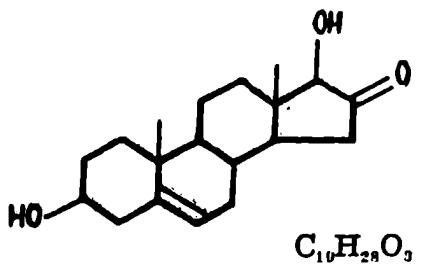
DERIVATIVES:

Diac. 218-9°(u); $[\alpha]_D^{20} = -135^\circ$ (CHCl₃): (1,2,3)

Diac.-oxime 226-35°: (4)

REFERENCES:

1. 71847
2. A18100
3. 55960
4. A58404

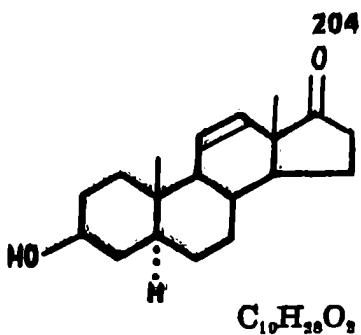
Δ^5 -ANDROSTENE-3(),17()-DIOL-16-ONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,2,3)**M.P.:** 197°: (1)**PHARMACOLOGY:****REMARKS:** May be 16-hydroxy-17-keto cpd. (1).**DERIVATIVES:**

Diac. 124-5°: (1,2,3)
 Oxime-3-ac. 244°: (1)
 3-ac. (+H₂O) 192°: (1)

REFERENCES:

1. 75055
2. A50999
3. A54229

Δ^{11} -ANDROSTENE-3(β)-OL-17-ONE



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.:

PHARMACOLOGY:

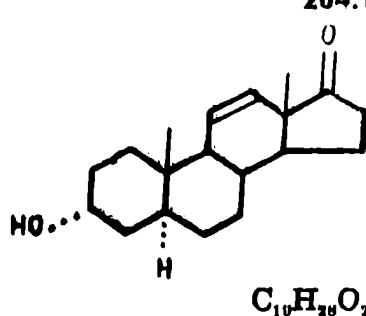
REMARKS: On the basis of unpublished work the position of the double bond at $\Delta^{9:11}$ appears more probable (2).

DERIVATIVES:

Ac. 102° ; $[\alpha]_D^{24} = +110.8^\circ \pm 4^\circ$ (acetone): (1)

REFERENCES:

1. 78817
2. A58412

Δ^{11} -ANDROSTENE-3(α)-OL-17-ONE

ISOLATION: Ur. (Human with Ad. Cortical tumor): (1).

STRUCTURE AND SYNTHESIS: (1)

M.P.: 181-3°: (1)

$[\alpha]_D^{26.0} = +122^\circ \pm 2^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS: Position of double bond uncertain (1).

DERIVATIVES:

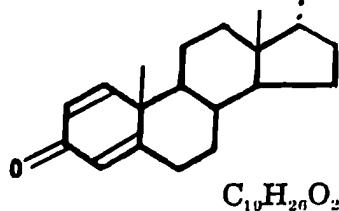
Ac. 178-80°; $[\alpha]_D^{23.6} = +114^\circ \pm 5^\circ$ (alc.): (1)

Bz. 162-4°: (1)

Semicarb. 279-80°: (1)

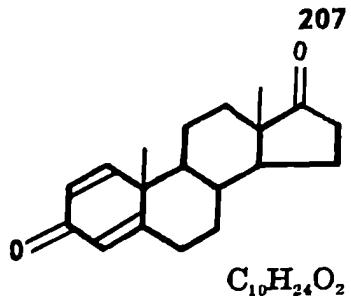
REFERENCES:

1. 81144

Δ^{14} -ANDROSTADIENE-3-ONE-17(α)-OL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:****PHARMACOLOGY:****REMARKS:****DERIVATIVES:****REFERENCES:**

1. A58705

Δ^{14} -ANDROSTADIENE-3,17-DIONE
 $(\Delta^1\text{-dehydro-}\Delta^4\text{-androstene-3,17-dione})$



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 168°(1)

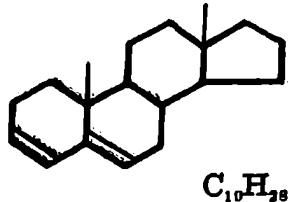
PHARMACOLOGY: Folliculoid in Allen-Doisy test: (1).

REMARKS:

DERIVATIVES:

REFERENCES:

1. A50839

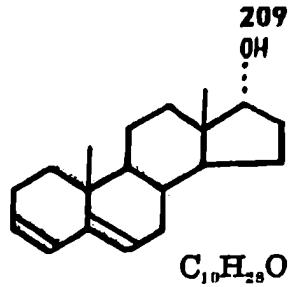
$\Delta^{4,5}$ -ANDROSTADIENE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:****PHARMACOLOGY:****REMARKS:****DERIVATIVES:**

3,17-di-Cl 127°: (1)

REFERENCES:

1. A54961

$\Delta^{4,5}$ -ANDROSTADIENE-17(α)-OL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 146°: (1)

PHARMACOLOGY: Testoid: 63: U. = 100 γ -C (1).

Anesthetic: 11: U. = 12 mg. of free cpd.; 15 mg. of ac. inact.-R (2).

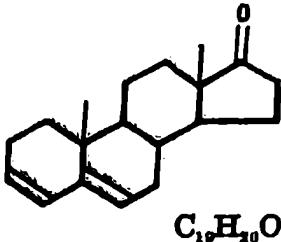
REMARKS:

DERIVATIVES:

Ac. 122-3°; $[\alpha]_D^{19} = -147.4^\circ$ (alc.): (1)

REFERENCES:

1. A9540
2. A36744

$\Delta^{8,8}$ -ANDROSTADIENE-17-ONE

ISOLATION: Ur. (human with Ad. tumor) : (1,4,5)
Ur. (♀ + ♂ human) : (1,5)

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 88-9°: (1,3,4)

$[\alpha]_D^{20} = -31.4^\circ$ (alc.): (1,4)

PHARMACOLOGY: Testoid: **63**: I.U. = ca. 350-400 γ -C (1).
Folliculoid: **2**: 1 mg. inact.-M (1).
Corticoid: **53A**: 1 mg./day inact.-R (1).
Anesthetic: **11**: 15 mg. inact.-R (3).

REMARKS: In ur. extracts cpd. may be artefact (4).

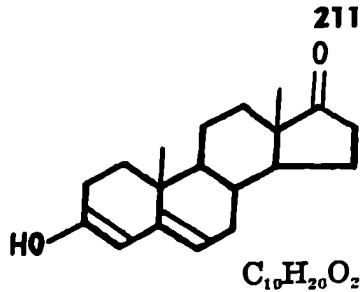
DERIVATIVES:

Oxime 164-70°: (1,4)

Semicarb. 291-2°: (1)

REFERENCES:

1. A8219
2. A9540
3. A36744
4. 81144
5. A56236

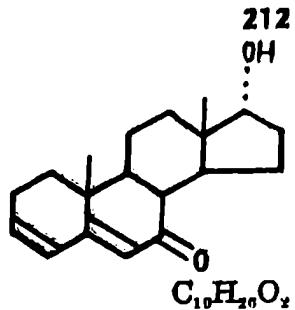
$\Delta^{4,5}$ -ANDROSTADIENE-3-OL-17-ONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:****PHARMACOLOGY:****REMARKS:****DERIVATIVES:**

Et. ether: (1)
16-iso-nitroso-et. ether: (1)

REFERENCES:

1. A56999

$\Delta^{4,5}$ -ANDROSTADIENE-7-ONE-17(α)-OL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 171-2°(u); (1,2)

$[\alpha]_D^{20} = -375^\circ$ (alc.); (1)

PHARMACOLOGY:

Testoid: 32A: 2 mg. inact.-C (1); 63: 100 γ /day inact.-C (1); 33: 3 mg./day inact.-R (1).

Folliculoid: 62: 2 mg./day inact.-M (1); 7: 2 mg./day inact.-R (1).

REMARKS:

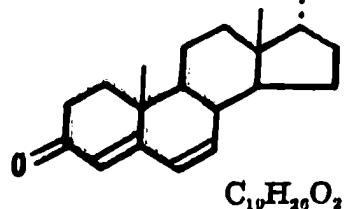
DERIVATIVES:

Ac. 222°(u); $[\alpha]_D^{20} = -400^\circ$ (CHCl₃); (1)

REFERENCES:

1. 71847
2. A18100

**$\Delta^{4,6}$ -ANDROSTADIENE-3-ONE-17(α)-OL
(Δ^4 -dehydro-testosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 209-11°: (1)

PHARMACOLOGY:

Testoid: 29: I.U. = ca. 200 γ of free cpd. and pr., > 200 γ of ac., and ca. 500 γ of bz.-C (1); **45:** "very slight act."-R (1).

Folliculoid: 1: 2 mg. inact.-Species? (1).

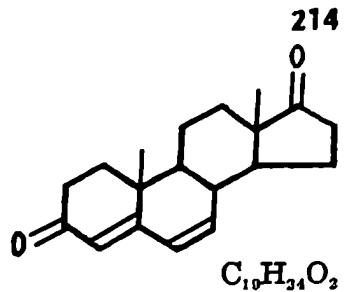
REMARKS:

DERIVATIVES:

Bz	$\left\{ \begin{array}{l} 257-60^\circ: \\ 246^\circ: \end{array} \right.$	(1)
Pr.	134°:	(2)
Ac.	143-4°:	(1)

REFERENCES:

1. 79620
2. 67266

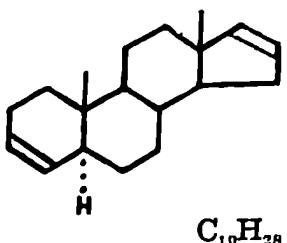
$\Delta^{4,6}$ -ANDROSTADIENE-3,17-DIONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (2)

M.P.: 173°: (2)

PHARMACOLOGY: **Testoid: 29:** I.U. = 1-2.5 mg.-C (13).
Folliculoid: 23: 2 mg. inact.-R (1).

REMARKS:**DERIVATIVES:****REFERENCES:**

1. 79620
2. 67266
3. A33511

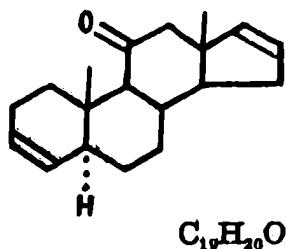
$\Delta^{8,16}$ -ANDROSTADIENE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)

M.P.: 30-8° (impure): (1)

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PHARMACOLOGY:**REMARKS:****DERIVATIVES:****REFERENCES:**

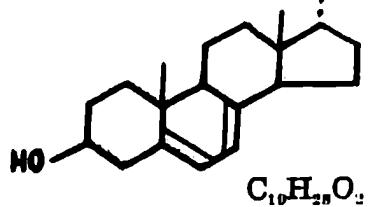
1. A8217

$\Delta^{8,16}$ -ANDROSTADIENE-11-ONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)

M.P.: 72-4°: (1)

PHARMACOLOGY:**REMARKS:****DERIVATIVES:****REFERENCES:**

1. A8217

$\Delta^{5,7}$ -ANDROSTADIENE-3(β),17(α)-DIOL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,2)

M.P.: 212°(u): (1)

PHARMACOLOGY: Testoid: 63: U. = 50 γ of diac.-C (1).

Folliculoid: 62: 1 mg./day of diac. act.-M (1); 7 : 0.5 mg./day of diac. act.-R (1).

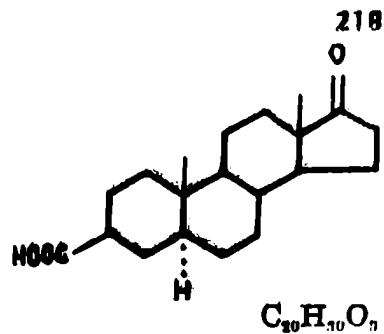
REMARKS:**DERIVATIVES:**

Diac.	132°(u); $[\alpha]_D^{23} = + 41^\circ$ (alc.):	(1)
Dibz.	{ 217-8°(u):	(1,3)
Peroxide-diac.	{ 211-13°:	(3)

REFERENCES:

1. 71847
2. 75062
3. A18100
4. 75056

**3(β)-CARBOXY-ANDROSTANE-17-ONE
(3-Carboxyandrostanone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 253°: (1)

PHARMACOLOGY:

Folliculoid: Test?: "The et. ester of this cpd. gave an estrous response in rats when given in quantities of from 5-10 γ . The et. ester is much more act. than the free acid." (1).

Testoid: Test?: "These cpds. were inact. when tested for male hormone properties by the cock's comb test in doses of 2 mg." (1).

REMARKS: Probably a mixture of 3- α and β .

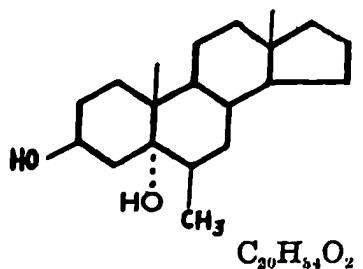
DERIVATIVES:

Et. ester 108-10°: (1)

Semicarb.-me.-ester 250-60°: (1)

REFERENCES:

- 1. A2295

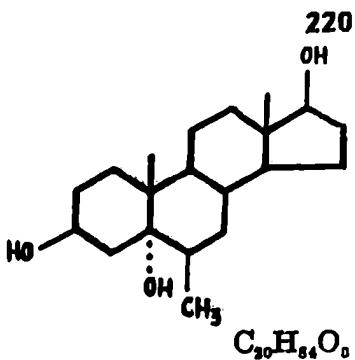
6()-METHYL-ANDROSTANE-3(),5(α)-DIOL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:****PHARMACOLOGY:****REMARKS:****DERIVATIVES:**

3-ac. 137-38°: (1)

REFERENCES:

1. A57000

6()-METHYL-ANDROSTANE-3(),5(α),17()-TRIOL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 117-20°: (1)

PHARMACOLOGY:

REMARKS:

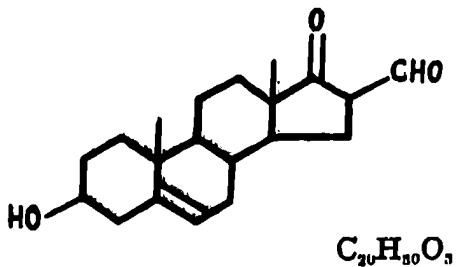
DERIVATIVES:

3,17-diac. 176-8°: (1)

REFERENCES:

1. A39609

**16()-FORMYL- Δ^5 -ANDROSTENE-3(β)-OL-17-ONE
(Formyl-dehydroisoandrosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 238-9°: (1)

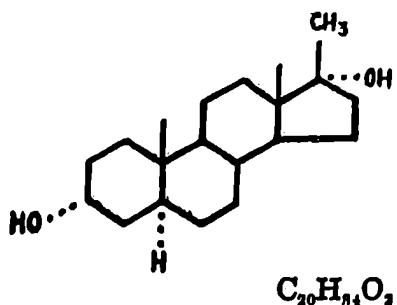
PHARMACOLOGY: Folliculoid: Test?: as act. as dehydroisoandrosterone-Species? (1).

REMARKS:

DERIVATIVES:

REFERENCES:

1. A34088

17(β)-METHYL-ANDROSTANE-3(α),17(α)-DIOL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)

M.P.: 184-5°: (1)

PHARMACOLOGY:

Testoid: **29:** I.U. = 35γ -C (3); **36:** I.U. = 25γ -C (4); **29:** U. = 25γ -C (1,2); **45:** s.ves. 150%/ 50γ , 370%/ 100γ , 650%/ 200γ ; pta. 44%/ 50γ , 105%/ 100γ , 250%/ 200γ -R (2,3,7,8); **37A:** "Methyl-androstanediol" s.ves. 290%/ 250γ , 740%/ 500γ , 1000%/ 750γ ; pta. 90%/ 250γ , 630%/ 500γ , 850%/ 1000γ -R (4).

Luteoid: **46:** "Methyl-androstanediol (cis)" + - + +/10-20 mg.-Rb. (6).

Folliculoid: **39A:** "Methyl-androstanediol" act.-R (9).

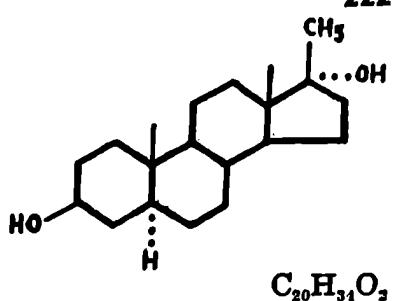
REMARKS: Assays on cpds. designated merely as "Methyl-androstanediol" are listed here.

DERIVATIVES:

Succinate 207-8°:
17¹-amine 204-6°; $[\alpha]_D^{20} = +4.5^\circ \pm 1^\circ$ (acetic acid):
Diac.-17¹-amine 207-8°:

REFERENCES:

- (1) 1. 33338
- (5) 2. 56783
- (5) 3. 54129
- 4. 56092
- 5. 80939
- 6. 67357
- 7. A33511
- 8. 56241
- 9. 55720

17(β)-METHYL-ANDROSTANE-3(β),17(α)-DIOL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:** 211-2°: (1)**PHARMACOLOGY:**

Testoid: **29**: I.U. = ca. 500 γ -C (1.5); **29**: U. = 350-400 γ -C (1.2); **45**: s.ves. 71%/200 γ , 510%/1000 γ ; pta. 51%/200 γ , 180%/1000 γ -R (2,5,6); **132**: at 2 mg. dose level s.ves. 2266(\pm 380)%; pta. 927(\pm 124)%; prep. gl. 220(\pm 48)%-R (3); **125**: at 2 mg. dose level, s.ves. 4050(\pm 227)%; pta. 1490(\pm 110)%; prep. gl. 298(\pm 36)%-R (3).

Luteoid: **46**: U. = < 200 mg.-Rb. (3).

Gonadotropic: **125**: Te. 119(\pm 22)%/2 mg.-R (3).

Anesthetic: **11**: U. => 15 mg.-R (3); **127**: U. = > 7 mg.-Fish (3).

REMARKS: Assays on cpds. designated merely as "Methyl-androstanediol" are listed with the 3(α),17(α) isomer.

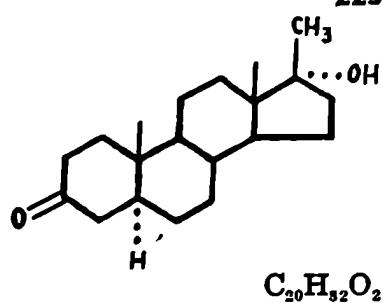
DERIVATIVES:

17 ¹ -amine	222-5°; $[\alpha]_D^{20} = -16.5^\circ \pm 1^\circ$ (acetic acid):	(4)
diac.-17 ¹ -amine	235°:	(4)
triac.-17 ¹ -amine	166°:	(4)

REFERENCES:

1. 54129
2. 56783
3. 100000
4. 80939
5. A33511
6. 56241

**17(β)-METHYL-ANDROSTANE-3-ONE-17(α)-OL
(17-Methyl-dihydro-testosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 192-3°: (1)

PHARMACOLOGY:

Testoid: **29:** I.U. = 15γ -C (1); **36:** I.U. = 24γ -C (3); **29:** U. = $11\text{-}15\gamma$ -C (1,2); **45:** s.ves. 170%/50 γ , 415%/100 γ , 900%/200 γ ; pta. 75%/50 γ , 210%/100 γ , 320%/200 γ -R (1,2,11); **37A:** s.ves. 230%/250 γ , 1850%/750 γ ; pta. 300%/250 γ , 1000%/750 γ -R (3); **37A:** act. on s.ves. > testosterone-R (4); **132:** at 2 mg. dose level, s.ves. $4266(\pm 260)\%$, pta. $1377(\pm 68)\%$, prep. gl. $220(\pm 54)\%$ -R (12); **96:** at 2 mg. dose level, s.ves. $5126(\pm 219)\%$; pta. $2514(\pm 185)\%$, prep. gl. $356(\pm 58)\%$ -R (12).

Folliculoid: **37B:** metrotropic and vag. cornifying act.-R (4); **39A:** "3-keto-17-methyl-androstanol" act.-R (6); **42:** 50-500 γ inact.-R (10).

Luteoid: **46:** + + + /7.5 mg.-Rb. (5); **46:** U. = < 200 mg.-Rb. (12).

Anesthetic: **11:** U. = 6 mg.-R (7); **127:** U. = 1 mg.-Fish (12).

REMARKS:

DERIVATIVES:

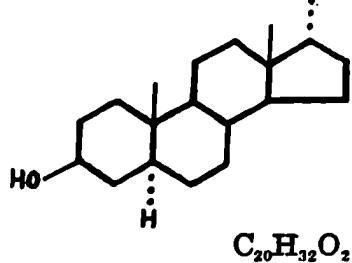
Semicarb. 235-6°: (1)

REFERENCES:

1. 54129
2. 56783
3. 56092
4. A9263
5. 67357
6. 55720
7. A36744
8. A38770
9. A38876
10. A57018
11. 56241
12. 100000

**17(α)-FORMYL-ANDROSTANE-3(β)-OL
 (17-formyl-androstane-3(β)-ol)**

ISOLATION:



STRUCTURE AND SYNTHESIS: (1)

M.P.: 92° + 143.5°: (1)

PHARMACOLOGY:

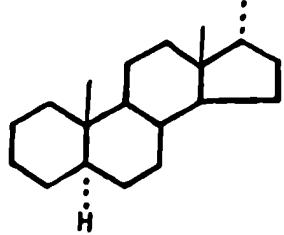
REMARKS:

DERIVATIVES:

REFERENCES:

1. 72132

**17(α)-CARBOXY-ANDROSTANE
(Etio-allo-cholic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3,4,5)

M.P.: 229-31°: (1,2,3,4)

PHARMACOLOGY:

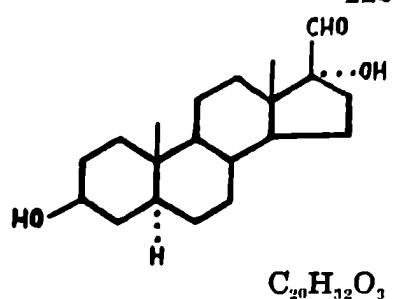
REMARKS:

DERIVATIVES:

Me. ester 143-4°: (3,4)

REFERENCES:

1. A54738
2. A54647
3. 76732
4. 78246
5. 79003

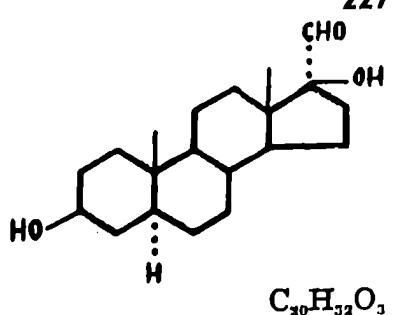
17(β)-FORMYL-ANDROSTANE-3(β),17(α)-DIOL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,2)**M.P.:****PHARMACOLOGY:****REMARKS:** Configuration assigned (2).**DERIVATIVES:**

Diac. 152-6°: (1)
 Diac.-semicarb (1)

REFERENCES:

1. 75676
2. 81147

**17(α)-FORMYL-ANDROSTANE-3(β),17(β)-DIOL
 (17 Formyl-androstanediol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 150-3°: (1)
 187-90°: (2)

$[\alpha]_D^{17} = -16.6^\circ \pm 5^\circ$ (alc.): (1)

PHARMACOLOGY:

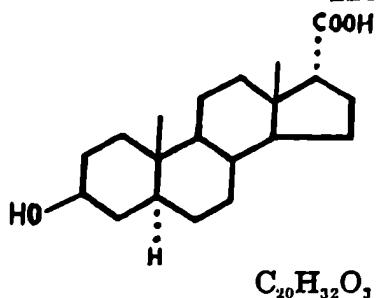
REMARKS:

DERIVATIVES:

REFERENCES:

1. 81149
2. 81695

**17(α)-CARBOXY-ANDROSTANE-3(β)-OL
(3(β)-hydroxy-*etio*-allo-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 247-9°: (2)
256-8°: (3)
250-2°: (4)

PHARMACOLOGY:

REMARKS:

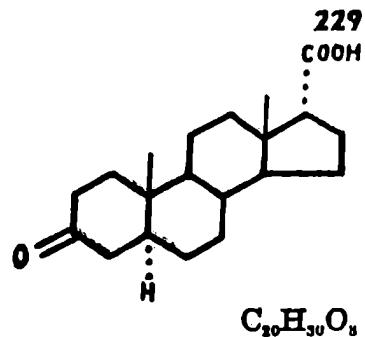
DERIVATIVES:

Me. ester	170-3°:	(1,2,3)
Bz.-me. ester	212°:	(2)
Ac.	247-9°:	(3,4)
Ac.-me. ester	142-4°:	(3)

REFERENCES:

1. 81790
2. 83012
3. A54647
4. 75893

**17(α)-CARBOXY-ANDROSTANE-3-ONE
(3-Keto- α -allo-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 253-6°: (2)
258-61°: (1)

PHARMACOLOGY:

REMARKS:

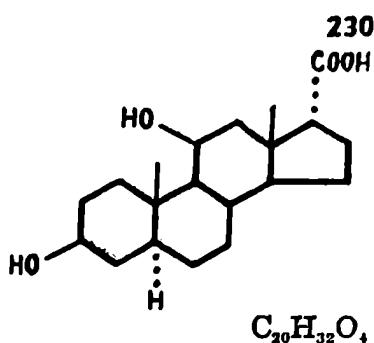
DERIVATIVES:

Me. ester 176-80°: (1,2)

REFERENCES:

1. 72132
2. A54647

**17(α)-CARBOXY-ANDROSTANE-3(β),11(β)-DIOL
(Kendall's acid "1C", 3,11-dihydroxy-*etio*-allo-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 284-6°(u): (1)

$[\alpha]_{5461}^{26} = +71^\circ \pm 3^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin (1).

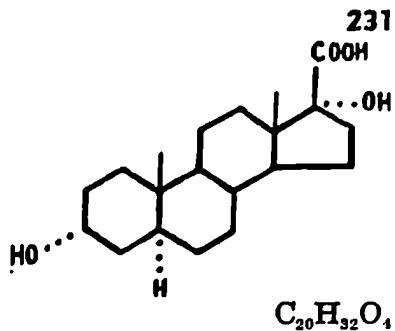
DERIVATIVES:

Monochlor acid 216°: (1)
Me. ester-monochlor acid 128-30°: (1)

REFERENCES:

1. 69294

17(β)-CARBOXY-ANDROSTANE-3(α),17(α)-DIOL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

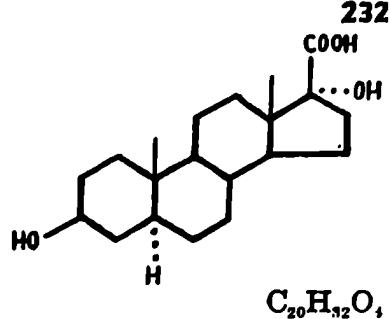
DERIVATIVES

17¹-nitril 163°: (1)
Diac.-17¹-nitril 183°: (1)

REFERENCES:

1. A57492

**17(β)-CARBOXY-ANDROSTANE-3(β),17(α)-DIOL
(3_t, 17_α-dihydroxy-*etio*-allo-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 260-2°: (3)

PHARMACOLOGY:

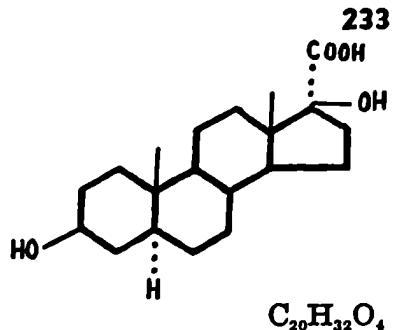
REMARKS: Me. ester not ppt. with digitonin (1).

DERIVATIVES:

Me. ester	213-4°; $[\alpha]_D^{20} = -1.3^\circ \pm 0.3^\circ$ (me. alc.):	(1,2)	1. 75747
3-ac.-me. ester	217°:	(1)	2. 83470
Diac.	228°:	(1)	3. A57492
17 ¹ -nitril	210°:	(3)	
Diac.-17 ¹ -nitril	144°:	(3)	

REFERENCES:

**17(α)-CARBOXY-ANDROSTANE-3(β),17(β)-DIOL
(3,17-dihydroxy-*etio*-allo-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 272-4°: (1)
277-8°: (2,3)

PHARMACOLOGY:

REMARKS: From Reichstein's cpd. "P." (2,3). Me. ester ppt. with digitonin (2).

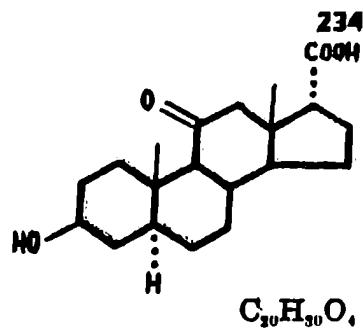
DERIVATIVES:

Me. ester 239-45°; $[\alpha]_{D}^{21} = +10.6^\circ \pm 2^\circ$ (me. alc.): (2)
Ac.-me. ester 184-6°; $[\alpha]_{D}^{20} = +7.09^\circ \pm 2^\circ$ (acetone): (4)

REFERENCES:

1. 76735
2. A19373
3. 75747
4. 75154

**17(α)-CARBOXY-ANDROSTANE-3(β)-OL-11-ONE
(Kendall's acid "1 B", 3-hydroxy-11-keto- α -etio-allo-cholic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 272-4°(u): (1)

$[\alpha]_{D}^{25} = +78^\circ \pm 2^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin (1).

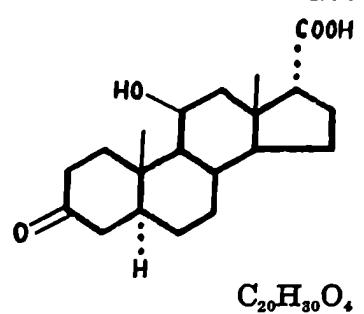
DERIVATIVES:

Ac. 210-13°: (1)
Me. ester 188-9°: (1)

REFERENCES:

1. 69294

**17(α)-CARBOXY-ANDROSTANE-3-ONE-11(β)-OL
(Kendall's acid "1 D", 3-keto-11-hydroxy-*etio*-allo-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 265-6°(u): (1)

$[\alpha]_{D}^{25} = +93^\circ \pm 2^\circ$ (alc.): (1).

PHARMACOLOGY:

REMARKS:

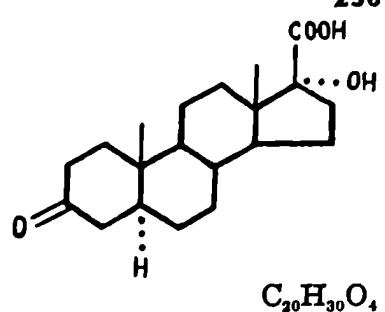
DERIVATIVES:

Me. ester 170-1° (u): (1)

REFERENCES:

1. 69294

**17(β)-CARBOXY-ANDROSTANE-3-ONE-17(α)-OL
 (3-keto-17(α)-hydroxy-*etio*-allo-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

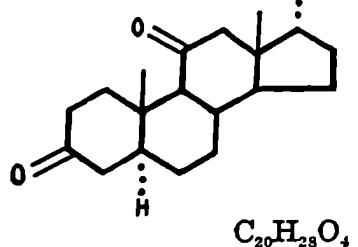
DERIVATIVES:

Me. ester 228-30°: (1)

REFERENCES:

1. 75152

17(α)-CARBOXY-ANDROSTANE-3,11-DIONE
(Kendall's acid "1 A", 3,11-diketo-*etio*-allo-cholanic acid)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 272-3° (u) : (1)
 280-5° + 292° : (2)
 286-90° : (2)
 279-82° : (3)

PHARMACOLOGY:

REMARKS:

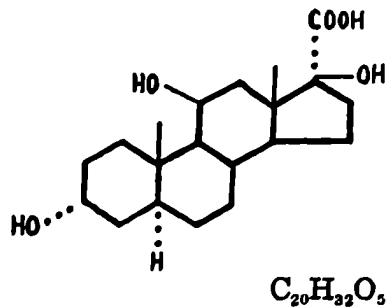
DERIVATIVES:

Mc. ester 200-1° (u) : (1)
 Mc. ester 207-10° : (2)

REFERENCES:

1. 09294
2. 73592
3. 72132

**17(α)-CARBOXY-ANDROSTANE-3(α),11(β),17(β)-TRIOL
 ($3(\alpha),11(\beta),17(\beta)$ -trihydroxy-*etio*-*allo*-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS:

M.P.:

PHARMACOLOGY:

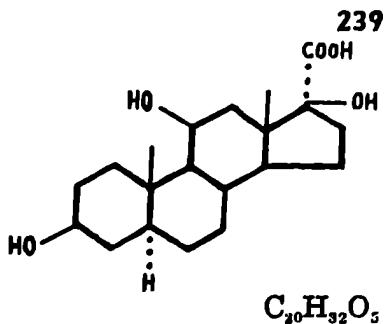
REMARKS:

DERIVATIVES:

Me. ester	$229\text{-}31^\circ$; $\{[\alpha]_{D}^{14} = +15^\circ \text{ (dioxane)} : (1)$ $[\alpha]_{5461}^{14} = +18^\circ \text{ (dioxane)} : (1)$	1. 83506
3-ac-me. ester	$186\text{-}7.5^\circ$; $\{[\alpha]_{D}^{15} = +19.5^\circ \text{ (dioxane)} : (1)$ $[\alpha]_{5461}^{15} = +23.9^\circ \text{ (dioxane)} : (1)$	

REFERENCES:

17(α)-CARBOXY-ANDROSTANE-3(β),11(β),17(β)-TRIOL
(acid from Kendall's cpd. "C", 3(β),11(β),17-(β)-trihydroxy-
etio-*allo*-cholanic acid)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 240-3°: (1)

$[\alpha]_{D}^{25} = +32.8^{\circ} \pm 3.3^{\circ}$ (alc.): (1)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin (1).

DERIVATIVES:

Me. ester 253-4°; $\{ [\alpha]_D^{13} = +7.6^{\circ}$ (dioxane) : (2)
 $[\alpha]_{5461}^{13} = +8.3^{\circ}$ (dioxane) : (2)

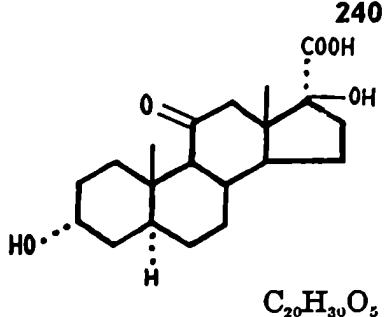
3-ac. of me. ester $\{ [\alpha]_D^{14} = +11.4^{\circ}$ (dioxane) : (2)
142-3° + 151-2°; $[\alpha]_{5461}^{14} = +5.1^{\circ}$ (dioxane) : (2)

REFERENCES:

1. 72169
2. 83506

**17(α)-CARBOXY-ANDROSTANE-3(α),17(β)-DIOL-11-ONE
($3\alpha,17\beta$ -dihydroxy-11-keto-etio-allo-cholanic acid)**

240



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

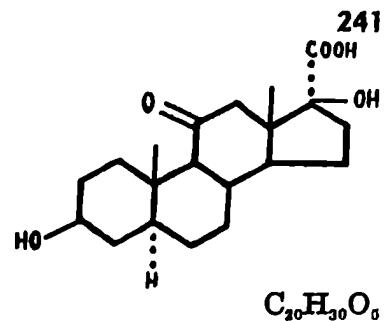
REMARKS:

DERIVATIVES:

3-ac-me ester $208-9^\circ$; $[\alpha]_{D}^{24} = +38^\circ$ (acetone); (1) 1. 83508
 $[\alpha]_{5461}^{14} = +47^\circ$ (acetone); (1) 2. 72169

REFERENCES:

17(α)-CARBOXY-ANDROSTANE-3(β),17(β)-DIOL-11-ONE
(Kendall's acid "5B", 3β,17β-dihydroxy-11-keto-*etio*-allo-cholanic acid)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 290-3° (u) : (1)
 298-301°: (2)

$[\alpha]_{5461}^{25} = +42.5^\circ \pm 2^\circ$ (me. alc.) : (1)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin (1).

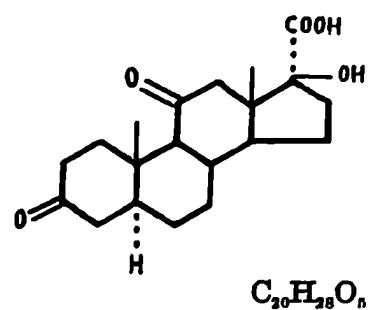
REFERENCES:

Diac.	259-60°; $[\alpha]_{5461}^{25} = -25.6^\circ \pm 1.8^\circ$ (alc.) : (1)
Me. ester	235-7°; $\left\{ \begin{array}{l} [\alpha]_{5461}^{16} = +29.3^\circ \text{ (dioxane)} : (2) \\ [\alpha]_D^{16} = +23.4^\circ \text{ (dioxane)} : (2) \end{array} \right.$
3-ac-me. ester	156-7°; $\left\{ \begin{array}{l} [\alpha]_D^{14} = +14.8^\circ \text{ (dioxane)} : (2) \\ [\alpha]_{5461}^{14} = +14.8^\circ \text{ (dioxane)} : (2) \end{array} \right.$

REFERENCES:

1. 72169
2. 83506

**17(α)-CARBOXY-ANDROSTANE-3,11-DIONE-17(β)-OL
(17β-hydroxy-3,11-diketo-*etio*-allo-cholanic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

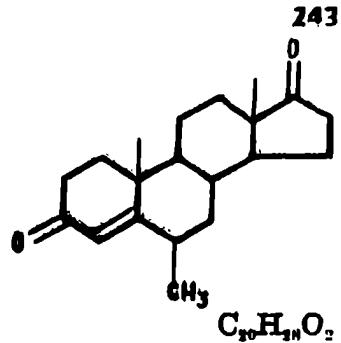
PHARMACOLOGY:

REMARKS:

DERIVATIVES:

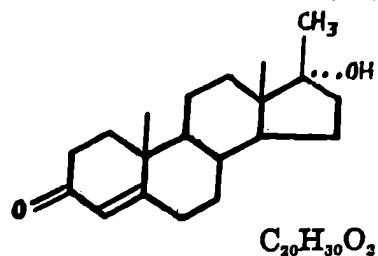
Me. ester 216-7°; $\left\{ \begin{array}{l} [\alpha]_D^{16} = +49.6^\circ \pm 5^\circ \text{ (dioxane)} : (1) 1. 83506 \\ [\alpha]_{5461}^{16} = +61.0^\circ \pm 2^\circ \text{ (dioxane)} : (1) \end{array} \right.$

REFERENCES:

6()-METHYL- Δ^4 -ANDROSTENE-3,17-DIONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)**M.P.:** 163.5-67°: (1)**PHARMACOLOGY:** Testoid: Test?: Act. in capon comb test ca. = that of Δ^4 -Androstene-3,17-dione (1).**REMARKS:****DERIVATIVES:****REFERENCES:**

1. A39609

**17(β)-METHYL-Δ⁴-ANDROSTENE-3-ONE-17(α)-OL
(17-methyl-testosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,6,13,14)

M.P.: 161-4.5°: (22)
163-4°: (1)

$[\alpha]_D = + 76.4^\circ$ (alc.): (22)

PHARMACOLOGY:

Testoid: **29**: I.U. = 25-30γ-C (6,24); **36**: I.U. = 80γ-C (3,4); **29**: U. = 15γ-C (7); **37A**: s.ves. 360%/
200γ; pta. 260%/200γ-R (3,4); **45**: s.ves. 135%/25γ, 290%/50γ, 680%/100γ, 1000%/200γ; pta.
63%/25γ, 105%/50γ, 200%/100γ, 360%/200γ-R (7,24,25); **31**: U. = ca. 0.5γ-C (5); **31**: 50γ/day
of triacetylglucuronate inact.-C (2); **37A**: on s.ves. less act. than testosterone-R (8); **128B**: prep.
gl. 238(± 27)%/1 mg.-R (19); **132**: at 2 mg. dose level, s.ves. 2620(± 148)%; pta. 855(± 35)%;
prep. gl. 175(± 32)%-R (35); **125**: at 2 mg. dose level, s.ves. 4359(± 135)%; pta. 1460(± 71)%;
prep. gl. 254(± 29)%-R (36); **69**: orally 2-4 \times less act. than parenterally — optimum dose 20-40
mg./day per os-Human (28,29,30,31,32,38).

Folliculoid: **37B**: very slight *metrotropic* and vag. cornifying act.-R (8); **38**: mitogenic and muci-
fying act. on vag.-R (9); **128C**: 2 mg./day vag. mucification or stratification-R (15); **39A**: 0.2-
1.5 mg./day *metrotropic* and slight vag. cornifying act.-R (26); **133B**: *Anti-Leydig* cell act.:
+ + +/1 mg., + + + +/10 mg.-R (23); **142**: *Anti-castration* cell act.: 200γ/day inact.-R (27);
74B: orally ca. 3 \times less act. than testosterone pr. parenterally—optimum dose 10-30 mg./day per
os-♀ Human (33); **128A**: *metrotropic* act.: 404(± 30)%/1 mg., *anti-castration* cell act.: + +/1
mg., + + +/4 mg.-R (19,34); **132**: *anti-castration* cell act.: + +/2 mg., + + +/10 mg.-R (34).

Anti-folliculoid: **129**: Hyp. 17(± 9)%/2 mg., 30(± 4)%/10 mg., Ad. 18(± 4)%/2 mg., 4(± 8)%/
10 mg.; Te. 43(± 3)%/2 mg., 66(± 7)%/10 mg.-R (16).

Gonadotropic: **21**: 0.25 mg. act.-X (10); **125**: Te. 143(± 26)%/2 mg.-R (36); **145**: 84%/13 mg.-M
(36).

Luteoid: **46**: I.U. = 30 mg.-Rb. 18); **46**: + - + +/7-20 mg.-Rb. (12); **54**: + + +/10 mg.-Rb. (12).

Corticoid: **146**: 2 mg. inact.-M (37).

Anesthetic: **11**: U. = 8 mg.-R (11); **127**: U. = 2.5 mg.-Fish (17).

REMARKS:

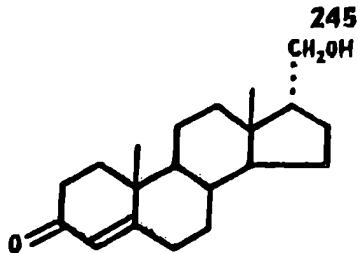
DERIVATIVES:

Triacetyl-glucuronic acid	186-9°; $[\alpha]_D^{20} = + 28.3^\circ$:	(2)	1. 54129	4. 56091
Semicarb.	226°:	(20)	2. 75626	5. 71314
Ac.	176-6.5°; $[\alpha]_D^{20} = + 69^\circ$ (alc.): (20)	3. 56092	6. A18098 .	

REFERENCES:

Ac.-semicarb.	238°:	(21)	7. 58733	23. A38086
Pr.	146°:	(21)	8. A9263	24. A38511
Pr.-semicarb.	230°:	(21)	9. 72400	25. 58241
			10. 75731	26. 55720
			11. A36744	27. 70000
			12. 67357	28. 80824
			13. A38939	29. A34366
			14. A39235	30. A36053
			15. A37486	31. A36059
			16. A37637	32. A36130
			17. A38070	33. A37636
			18. A56335	34. A37513
			19. A56752	35. A38071
			20. 75740	36. 100000
			21. A54646	37. A36403
			22. 67872	38. A37108

**17(α)-[HYDROXYMETHYL]- Δ^4 -ANDROSTENE-3-ONE
(Δ^4 -hydroxy-methylandrostene-3-one)**



ISOLATION:

C₂₀H₃₀O₂

STRUCTURE AND SYNTHESIS: (1)

M.P.: 158-9°: (1)

PHARMACOLOGY: Testoid: 45: inact. up to 0.1 mg. daily-R (2).

REMARKS:

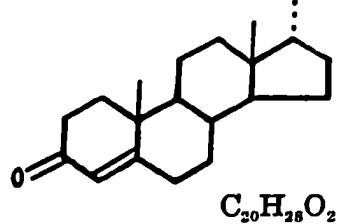
DERIVATIVES:

Ac. 114-5°: (1)
Ac.-semicarb. 214-5°: (1)

REFERENCES:

1. 79625
2. 79621

**17(α)-FORMYL- Δ^4 -ANDROSTENE-3-ONE
(20-nor-progesterone, 17-formyl- Δ^4 -androstene-3-one)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 151-3°: (2)

$[\alpha]_D^{10} = +159^\circ$ (dioxane): (2)

PHARMACOLOGY: Testoid: 29: I.U. = 1 mg.-C (3).

Luteoid: 86A: up to 5 mg. inact.-Rb. (2); slightly act. at 10-20 mg.-Rb. (3).

REMARKS:

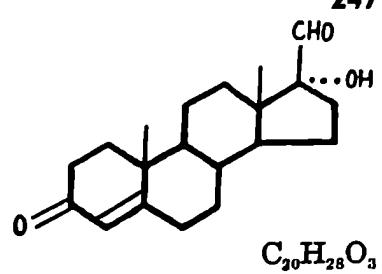
DERIVATIVES:

Disemicarb. 296°: (2)

REFERENCES:

1. 79625
2. 79621
3. 79623

**17(β)-FORMYL- Δ^4 -ANDROSTENE-3-ONE-17(α)-OL
 (17-formyl- Δ^4 -androstene-3-one-17-ol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 133-5°: (1)

$[\alpha]_D^{13} + 80.8^\circ \pm 2^\circ$ (acetone): (1)

PHARMACOLOGY:

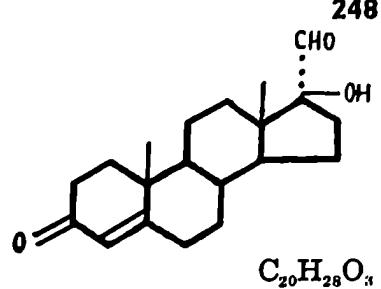
REMARKS:

DERIVATIVES:

REFERENCES:

1. 81695

**17(α)-FORMYL- Δ^4 -ANDROSTENE-3-ONE-17(β)-OL
 (17 Formyl- Δ^4 -androstene-3-one-17-ol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 142-6°: (1)
 162-4°: (2)

$[\alpha]_D^{15} = +49.4^\circ \pm 3^\circ$ (acetone): (1)
 $[\alpha]_D^{13} = +47.7^\circ \pm 2^\circ$ (acetone): (2)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

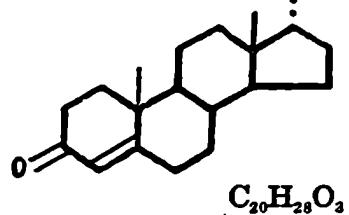
Semicarb. > 350°: (1)

REFERENCES:

1. 81149
2. 81695

249
COOH

17(α)-CARBOXY- Δ^4 -ANDROSTENE-3-ONE
(Δ^4 -3-keto-androstanic acid)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 236-42°: (4)
258-62°: (1)
256-60°: (2)

PHARMACOLOGY: Anesthetic: 11: 20 mg. inact. and toxic-R (5); 127: 7 mg. inact.-Fish (5).

REMARKS:

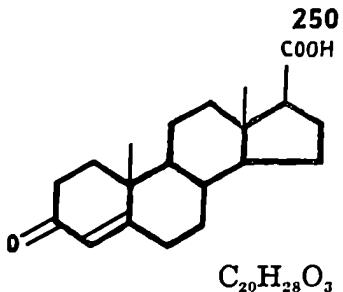
DERIVATIVES:

Me. ester { 130-1°: (4)
 { 134-5°: (1,3)

REFERENCES:

1. 79625
2. 79621
3. 83012
4. A54647
5. 100000

**17(β)-CARBOXY-Δ⁴-ANDROSTENE-3-ONE
(17-iso-3-keto-Δ⁴-etiochenic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 194-6°: (1)

$[\alpha]_D^{18} = +47.5^\circ \pm 2^\circ$ (acetone): (1)

$[\alpha]_{5461}^{10} = +54^\circ \pm 3^\circ$ (acetone): (1)

PHARMACOLOGY:

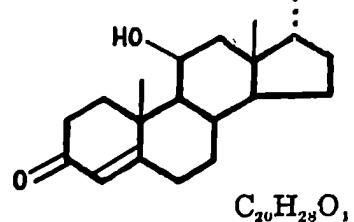
REMARKS:

DERIVATIVES:

Me. ester 115-6°; $[\alpha]_D^{18} = +36^\circ \pm 2^\circ$ (acetone): (1) 1. 79195
 $[\alpha]_{5461}^{10} = +46^\circ \pm 3^\circ$ (acetone): (1)

REFERENCES:

**17(α)-CARBOXY- Δ^4 -ANDROSTENE-3-ONE-11(β)-OL
(Kendall's "acid 2")**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 253-8°(u): (1)

$[\alpha]_{D}^{25} = +218^\circ \pm 2^\circ$ (alc.): (1)

PHARMACOLOGY:

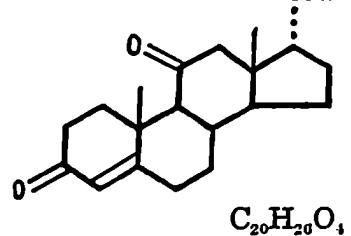
REMARKS:

DERIVATIVES:

REFERENCES:

1. 69294

**17(α)-CARBOXY- Δ^4 -ANDROSTENE-3,11-DIONE
(Kendall's "acid 1")**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 267-9°(u): (2)
268-70°: (1)
266-72°: (3)

$[\alpha]_{5461}^{25} = + 291^\circ$ (alc.): (2)
 $[\alpha]_{5461}^{25} = + 290^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

Mc. ester 178-9°(u); $[\alpha]_{5461}^{25} = + 299^\circ$: (2,3)
Oxime 258-60°: (2)

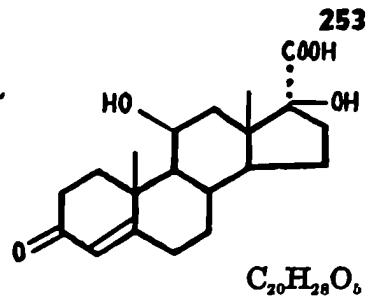
REFERENCES:

1. 72170
2. 69294
3. A9075

**17(α)-CARBOXY- Δ^4 -ANDROSTENE-3-ONE-11(β),17(β)-DIOL
(11 β ,17 β -dihydroxy-3-keto- α -etio-cholene-4-acid)**

253

ISOLATION:



STRUCTURE AND SYNTHESIS: (1)

M.P.: 235-45°: (1)

PHARMACOLOGY:

REMARKS:

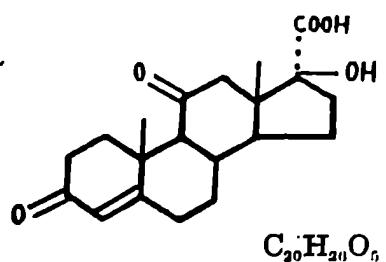
DERIVATIVES:

Me. ester $207-8^\circ$ $[\alpha]_{D}^{14} = +111.5^\circ \pm 2^\circ$ (dioxane): (1)
 $[\alpha]_{5461}^{14} = +135.2^\circ \pm 2^\circ$ (dioxane): (1)

REFERENCES:

1. 83508

**17(α)-CARBOXY- Δ^4 -ANDROSTENE-3,11-DIONE-17(β)-OL
 (3,11-diketo-17(β)-hydroxy- Δ^4 -etiochenic acid; Kendall's "acid 5")**



ISOLATION:

STRUCTURE AND SYNTHESIS:

M.P.:

PHARMACOLOGY:

REMARKS:

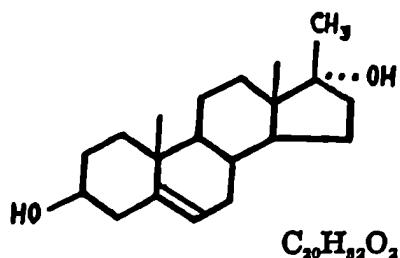
DERIVATIVES:

A.c. 239-43°; $[\alpha]_{D461}^{25} = +118.5 \pm 2^\circ$ (alc.): (1)

REFERENCES:

1. 72169

17(β)-METHYL- Δ^5 -ANDROSTENE-3(β),17(α)-DIOL
(Methyl-trans-androstene-diol)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 204°: (1)

PHARMACOLOGY:

Testoid: **29:** I.U. = 650γ -C (1); **36:** I.U. = 155γ of "Methyl-trans-androstenediol"-C (2); **29:** I.U. = ca. 500γ -C (8); **29:** U. = 350 - 450γ -C (1,3); **45:** s.ves. 57%/100γ, 150%/200γ; pta. 19%/100γ, 75%/200γ-R (1,5,8); **37A:** "Methyl-trans-androstenediol" s.ves. 29%/250γ, 830%/750γ; pta. 43%/250γ, 450%/750γ-R(2); **132:** at 2 mg. dose level, s.ves. $3017(\pm 124)\%$; pta. $955(\pm 44)\%$; prep.gl. $290(\pm 39)\%$ -R (9); **33:** U. = 2 mg.-R (11).

Folliculoid: **23,24:** vag. opening, cornification and metrotropic act.-R(5).

Luteoid: **46:** "Methyl-trans-androstenediol" "10 mg. showed only slight signs of act."-Rb.(6); **46:** I.U. = 30 mg.-Rb.(9).

Anti-folliculoid: **129:** Hyp. $7(\pm 7)\%$ /1 mg., Ad. $11(\pm 3)\%$ /1 mg., Te. $54(\pm 7)\%$ /1 mg.-R(9).

Anesthetic: **11:** U. = 20 mg.-R.(9); **127:** U. = > 7.0 mg.-Fish(9).

Corticoid: **146:** 2 mg. of "Methylandrostenediol" inact.-M(10).

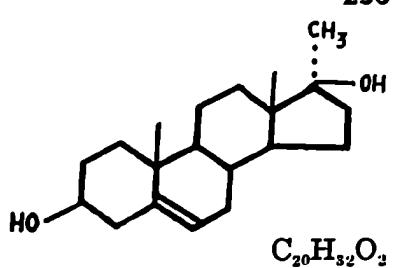
REMARKS:

DERIVATIVES:

Diac.	145 - 6° ; $[\alpha]_D^{21} = -59^\circ$ (alc.): (7)	1. 54129
17-ac.	164° : (4)	2. 56002
Dipr.	83° : (4)	3. 56783
17-pr.	138° : (4)	4. A54646 5. 56241 6. 67357 7. 75740 8. A33511 9. 100000 10. A36403 11. A92

REFERENCES:

**17(α)-METHYL- Δ^5 -ANDROSTENE-3(β),17(β)-DIOL
 $(\Delta^5\text{-}17\text{-iso-methyl-androstene-3-trans-17-cis-diol})$**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 203-4°: (1)

$[\alpha]_D^{21} = -81^\circ$ (alc.) ; -84.5° (CHCl_3): (1)

PHARMACOLOGY:

REMARKS: Does not form diac.: (1)

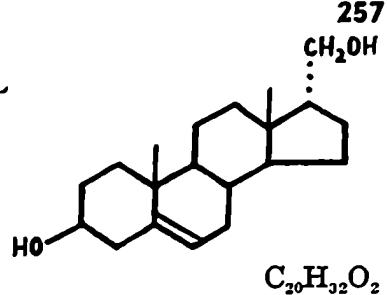
DERIVATIVES:

3-ac. 160-1°; $[\alpha]_D^{22} = -77^\circ$ (alc.): (1)

REFERENCES:

1. 75740

**17(α)-[1-HYDROXYMETHYL]- Δ^5 -ANDROSTENE-3(β)-OL
 $(\Delta^5$ -hydroxy-methyl-androstene-3-ol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 209-11°: (1)

PHARMACOLOGY: Testoid: 29: 2 mg. inact.-C (2); 45: 1 mg./day inact. on s.ves. and pta.-R (2).

REMARKS:

DERIVATIVES:

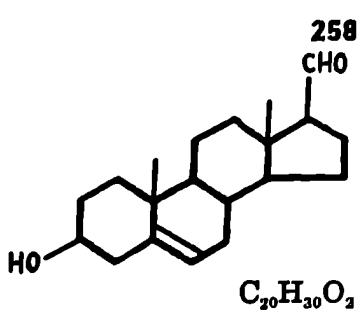
Diac. 136-7°: (1,2)

REFERENCES:

1. 79025
2. 70621

**17()FORMYL- Δ^5 -ANDROSTENE-3(β)-OL
(17-formyl- Δ^5 -androstene-3-ol; 20-nor-pregnolone)**

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CHO



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 130° + 148-53°: (1)

$[\alpha]_D^{21} = -14.5^\circ$ (CHCl₃): (1)

PHARMACOLOGY:

REMARKS:

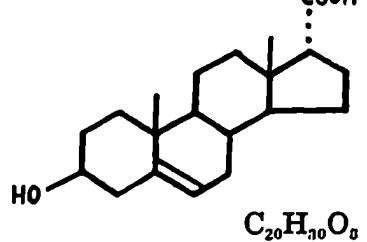
DERIVATIVES:

Ac.	169-71°; $[\alpha]_D^{23} = -13.5^\circ \pm 4^\circ$ (CHCl ₃): (1)
Semicarb.	226-8°: (1)
2:4-dinitrophenylhydrazone	207-9°: (1)
Dime.acetal	185-9°: (1)

REFERENCES:

1. 79623

**17(α)-CARBOXY- Δ^5 -ANDROSTENE-3(β)-OL
(3-hydroxy- Δ^5 -Etiochenic acid, 3β-hydroxy-etio-5-cholenic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3,4,5)

M.P.: 276°: (1)
284-6°: (2)
273-4°: (4)
280-1°: (5)

PHARMACOLOGY:

REMARKS:

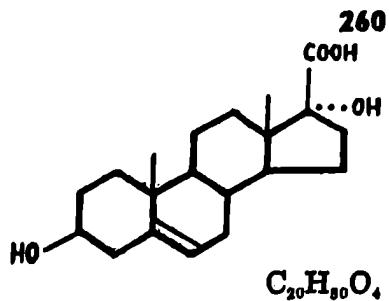
DERIVATIVES:

Ac.	242°; $[\alpha]_D^{10} = -19.9^\circ$ (acetone): (1,5)
Me. ester	181-2°: (2,5)
3 ac.-me. ester	158-60°: (2,5)
Ac. acidchloride	165°: (2)

REFERENCES:

1. 72716
2. A9077
3. 83012
4. 83550
5. A54647

**17(β)-CARBOXY-Δ⁵-ANDROSTENE-3(β),17(α)-DIOL
(Δ⁵-3,17-dihydroxy-ethio-cholenic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 267-8°: (1)
260-1°: (2)

PHARMACOLOGY:

REMARKS: Me. ester not ppt. with digitonin: (3). The 3 ac. of nitriles I and II are 17 epimers (4)

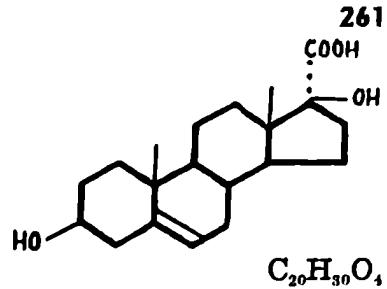
DERIVATIVES:

Amide	294-6°: (1)
3-ac.-amide	269-70°: (1)
3-ac.	200-1°: (1)
Me. ester	191-2°: (1,2)
Diac.	220°: (1,2)
Diac.-me. ester	144-5°: (1,2)
3-ac.-me. ester	163-4°: (2)
Nitrile	210-50°: (4)
Diac.-nitrile	{ 207-8°: (4) { 215-7°: (1)
3-ac.-nitrile	{ I 195°: (4) { II 203-6°: (4)

REFERENCES:

1. 75751
2. A15310
3. A19373
4. 72716

**17(α)-CARBOXY- Δ^5 -ANDROSTENE-3(β),17(β)-DIOL
 ($3\beta,17\beta$ -dihydroxy- Δ^5 -etio-cholenic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 247-9°: (2)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

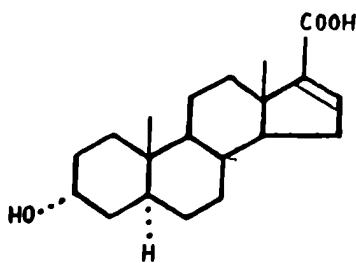
Me. ester 238-40°; $[\alpha]_D^{10} = -61.9^\circ \pm 10^\circ$ (acetone): (2)

REFERENCES:

1. 81791
2. 75154

**17-CARBOXY- Δ^{10} -ANDROSTENE-3(α)-OL
(Δ^{10} -3(α)-hydroxy-*etio*-allo-cholenic acid)**

262



C₂₀H₃₀O₂

ISOLATION:

STRUCTURE AND SYNTHESIS:

M.P.:

PHARMACOLOGY:

REMARKS:

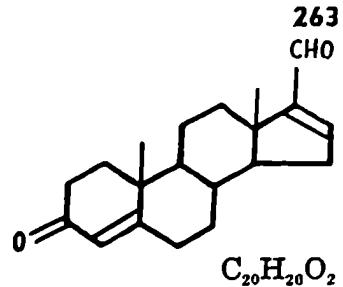
DERIVATIVES:

3-ac-17¹-nitril. 198-200°: (1)

REFERENCES:

1. A57490

**17-FORMYL- $\Delta^{4,10}$ -ANDROSTADIENE-3-ONE
[17-Formyl-androstadiene-(4,16)-one-(3)]**



ISOLATION:

STRUCTURE AND SYNTHESIS:

M.P.: 154-6°: (1)

$[\alpha]_D^{19} = +13.4^\circ \pm 2^\circ$ (acetone): (1)

PHARMACOLOGY:

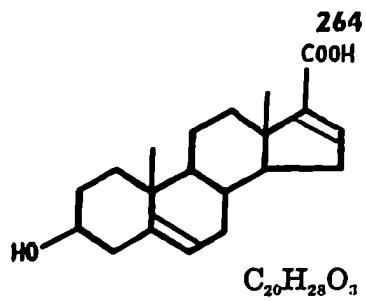
REMARKS: Structure uncertain.

DERIVATIVES:

REFERENCES:

- 1. 83470

**17-CARBOXY- $\Delta^{5,10}$ -ANDROSTADIENE-3(β)-OL
 ($\Delta^{5,10}$ -Etio-choladiene carbonic acid; 3(β)-hydroxy-etio-
 5,10-choladienic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 256° (u) : (1)
 255-7° (2)

PHARMACOLOGY:

REMARKS:

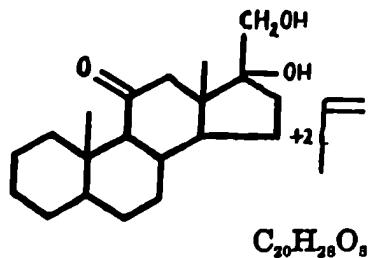
DERIVATIVES:

Ac.	253-4°: (1)
17 ¹ -nitrile	176°: (3)
3-ac.-17 ¹ -nitrile	210°: (1,3)

REFERENCES:

1. 72716
2. 83559
3. 75054

(Cafestanol)



ISOLATION: Coffee: (2,3,4,5,6,7)

STRUCTURE AND SYNTHESIS: (1,3,4,5,6,7,8)

M.P.: 155-7°: (2,3)
160-2°: (4)

$[\alpha]_D = -140^\circ$ (CHCl_3): (2,3)
 $[\alpha]_D^{20} = -107^\circ \pm 2^\circ$ (CHCl_3): (4)

PHARMACOLOGY:

Folliculoid: 62: U. = 2.5 mg., higher doses toxic-M (2); 1: 30 mg. of ac. inact. and toxic-R (4).
Testoid: Test?: 300 mg. inact. in δ/c R (2).

REMARKS: Structure as given in heading suggested by (1). Cpd. probably contains 2 double bonds (2,3). May be etiocholane cpd. Ancient literature see (4). "Kahwed" probably impure prep. of same. Steroid nature very doubtful (8).

DERIVATIVES:

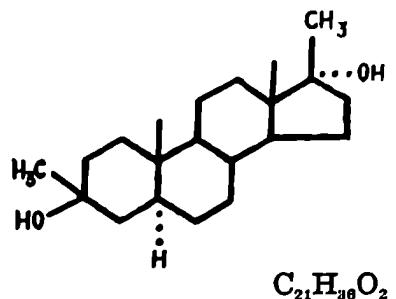
Monoac	$\{164-6^\circ; [\alpha]_D = -135^\circ$ (CHCl_3): (1,2,3)
	$\{169-71; [\alpha]_D = -100^\circ$ (CHCl_3): (4)
Several derivatives of unknown constitution:	(4)
Anhydro cpd.	126-8°: (3)
Anhydro semicarb cpd.	227-9°: (3)
Ac.-hexahydro cpd.	101-5°: (3)
Octahydro-anhydro cpd.	(3)

REFERENCES:

1. A34116
2. A34253
3. A34254
4. 83020
5. A54243
6. A54244
7. A54245
8. 83714

3(),17(β)-DIMETHYL-ANDROSTANE-3(),17(α)-DIOL

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ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 150° (not sharp) : (1)

PHARMACOLOGY: Testoid: 29: 500 γ not act.-C (1).

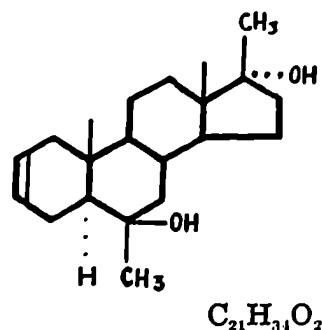
REMARKS: Perhaps a mixture of isomers (1).

DERIVATIVES:

REFERENCES:

1. 33338

6(),17(β)-DIMETHYL-Δ²-ANDROSTENE-6(),17(α)-DIOL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 80-85° (+ H₂O) : (1)

PHARMACOLOGY:

REMARKS: Position of double bond uncertain.:

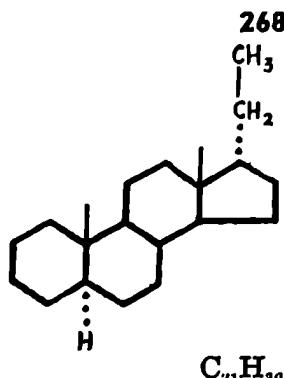
DERIVATIVES:

REFERENCES:

1. A57000

**17(α)-ETHYL-ANDROSTANE
(allo-pregnane)**

268



ISOLATION:

STRUCTURE AND SYNTHESIS: (2,3)

M.P.: 84-5°: (1,2,3,4,5)
81-82.5°: (6)

$[\alpha]_D^{21} = +12.7^\circ$ (CHCl₃): (3)
 $[\alpha]_D = +18^\circ \pm 1^\circ$ (CHCl₃): (1)

PHARMACOLOGY:

Folliculoid: 55: vag. stratification with 20 mg.-R (6).

Anesthetic: 11: 20 mg. inact.-R (7).

REMARKS:

DERIVATIVES:

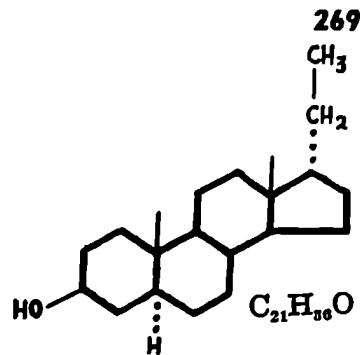
REFERENCES:

1. 77144
2. 72132
3. 72134
4. 72920
5. 72108
6. A37486
7. A38070

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**17(α)-ETHYL-ANDROSTANE-3(β)-OL
(allo-pregnanol-3)**

ISOLATION:



STRUCTURE AND SYNTHESIS: (1)

M.P.: 137-8°: (1)

$[\alpha]_D = +16^\circ \pm 1^\circ$ (CHCl₃): (1)

PHARMACOLOGY:

REMARKS:

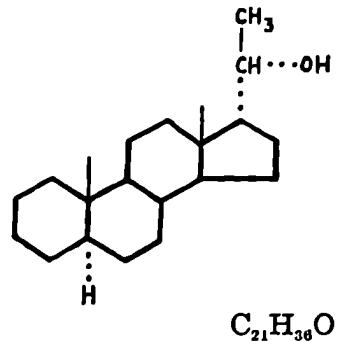
DERIVATIVES:

Ac. 115-6°: (1)

REFERENCES:

1. 77144

**17(α)-[1(α)-HYDROXYETHYL]-ANDROSTANE
(allo-pregnanol-20)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 136°: (1)

PHARMACOLOGY:

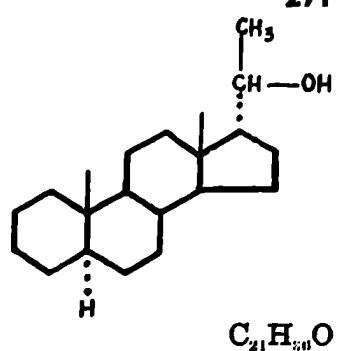
REMARKS:

DERIVATIVES:

Ac. 94°: (1)

REFERENCES:

1. 75328

17(α)-[1(β)-HYDROXYETHYL]-ANDROSTANE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)

M.P.: 140°: (1)

PHARMACOLOGY:**REMARKS:****DERIVATIVES:**

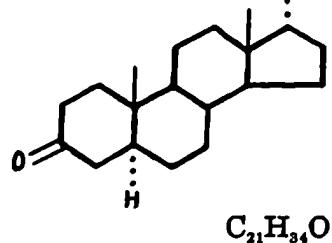
Ac. 156°: (1)

REFERENCES:

1. 75328

272
CH₃
CH₂

17(α)-ETHYL-ANDROSTANE-3-ONE
(allo-pregnane-3)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 116-7°: (1)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

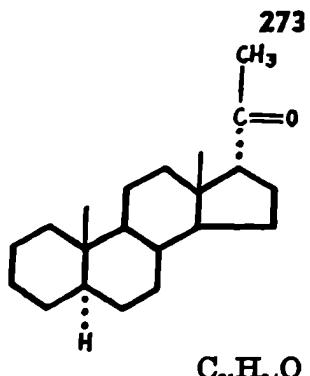
Semicarb. 230°: (1)
Hydrazone 226°: (1)

REFERENCES:

1. 77144

**17(α)-[1-KETOETHYL]-ANDROSTANE
(allo-pregnane-20)**

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ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 129°: (1)
132°: (2)
130-2°: (3)
134°: (4)

PHARMACOLOGY:

REMARKS:

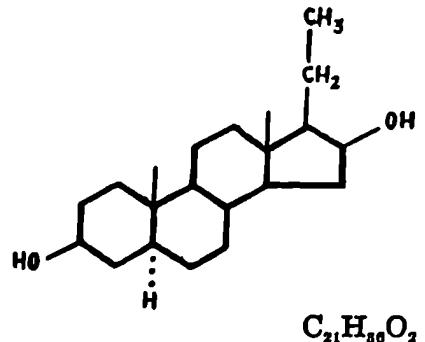
DERIVATIVES:

Semicarb. 260°: (1)
2:4-dinitrophenylhydrazone 220-3°: (1)
17-Br. 127-9°: (2)
17,17²-dibr. 128-30°: (2)

REFERENCES:

1. 75328
2. 83009
3. 83008
4. A54002

**17()-ETHYL-ANDROSTANE-3(),16()-DIOL
(allo-pregnane-3(),16()-diol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 255°: (1)

PHARMACOLOGY:

REMARKS:

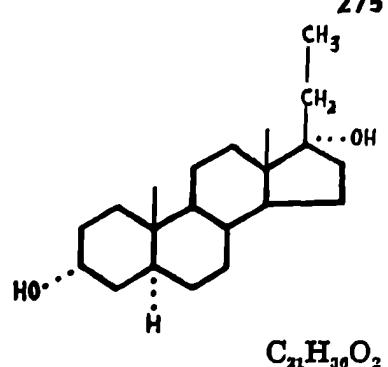
DERIVATIVES:

Diac. 140°: (1)

REFERENCES:

1. 75333

17(β)-ETHYL-ANDROSTANE-3(α),17(α)-DIOL
(cis-ethyl-androstanediol)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 143-4°: (1,2)

PHARMACOLOGY:

Testoid: **29**: I.U. = ca. 50γ-C (5); **29**: U. = 25γ-C (1,2); **45**: s.ves. 43%/100γ, 165%/200γ, 560%/500γ, pta. 58%/100γ, 100%/200γ, 240%/500γ-R (2,5).

Luteoid: **46**: "Ethylandrostanediol (cis)" + to + +/10 mg.,? Slight /20 mg.-Rb. (4).

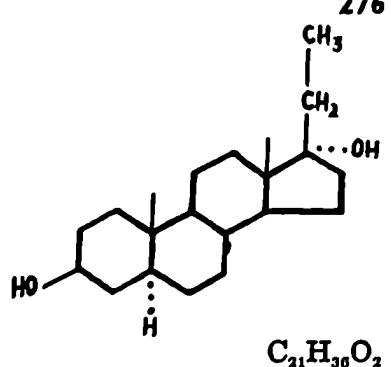
Gonadotropic: **21**: "Ethyl-cis-androstanediol" inact.-X (3).

REMARKS:

DERIVATIVES:

REFERENCES:

1. 54129
2. 56783
3. 75731
4. 67357
5. A33511

17(β)-ETHYL-ANDROSTANE-3(β),17(α)-DIOL**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,4)

M.P.: 204-5°: (1,3)
221-2°: (4)

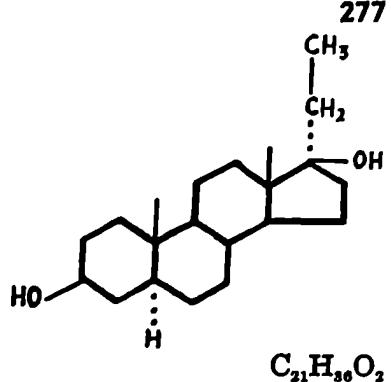
PHARMACOLOGY: Testoid: **29**: I.U. = 550γ -C (1); **29**: U. = 400γ -C (2); **45**: s.ves. inact. at 200γ , 75%/500 γ ; pta. inact. at 200γ , 28%/500 γ -R (1,2,5).

REMARKS: Not ppt. by digitonin: (4).

DERIVATIVES:**REFERENCES:**

1. 54129
2. 56783
3. 83470
4. A19373
5. A33511

17(α)-ETHYL-ANDROSTANE-3(β),17(β)-DIOL
 (allo-pregnaneol-3-trans-17(β))



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 174 + 187°: (1)

PHARMACOLOGY:

REMARKS: Ac. ppt. by digitonin: (1)

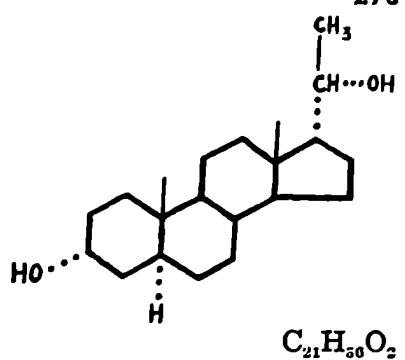
DERIVATIVES:

3-ac. 174-8°; $[\alpha]_D^{10} = -20.05^\circ \pm 2^\circ$ (acetone): (1) 1. 75154

REFERENCES:

**17(α)-[1(α)-HYDROXYETHYL]-ANDROSTANE-3(α)-OL
(epi-allo-pregnaneol)**

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ISOLATION: Ur. (bull) : (2)
Ur. (preg. mare) : (5)
Ur. (preg. cow) : (1)
Ur. (preg. human) : (4,5,6)

STRUCTURE AND SYNTHESIS: (1)

M.P.: 243°: (1,2)
243-5°: (6)
248°: (7)

$[\alpha]_D^{20} = +17^\circ$ (alc.) : (6)
 $[\alpha]_{5461}^{20} = +20^\circ$ (alc.) : (6)

PHARMACOLOGY: Corticoid: **53A**: "Allo-pregnadiol" inact. up to 15 mg.-R (3).
Folliculoid: **60**: Act. of "allopregnadiols" < 'olones < 'diones-B (4).

REMARKS:

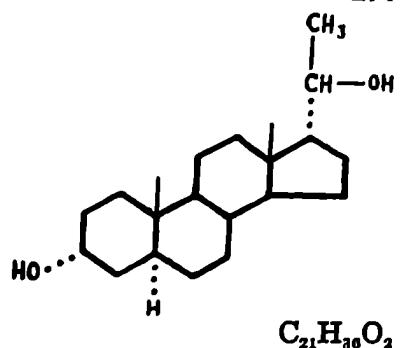
DERIVATIVES:

Diac. 141°; $[\alpha]_D^{20} + 18^\circ$ (benzene) : (2,6,7)
 $[\alpha]_{5461}^{20} + 21^\circ$ (benzene) : (6)

REFERENCES:

1. 72029
2. 73730
3. 75903
4. A30097
5. 76880
6. 67685
7. 31041

**17(α)-[1(β)-ETHYL]-ANDROSTANE-3(α)-OL
(3-*epi*-allo-pregnaneol-20-trans)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 205-7°: (1)

PHARMACOLOGY:

REMARKS:

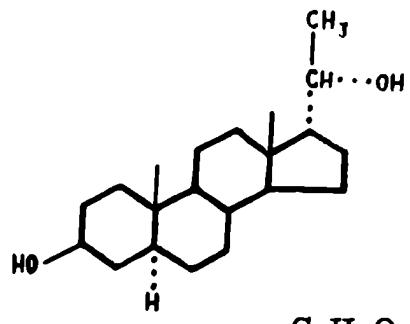
DERIVATIVES:

Diac. 124°: (1)

REFERENCES:

- 1. A6244

**17^(\alpha)-[1^(\alpha)-ETHYL]-ANDROSTANE-3^(\beta)-OL
(allo-pregnane-3^(\beta),20^(\alpha)-diol)**



ISOLATION: Ur. (bull): (5)
Ur. (preg. mare): (3,7)
Ur. (preg. human): (7,8)
Ur. (preg. cow): (4)

STRUCTURE AND SYNTHESIS: (1,2,3,4,5,6,7,8)

M.P.: 215°: (5)
214°: (4)
218°: (2)
214-7°: (1,6)
216°: (3,8)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin: (4)

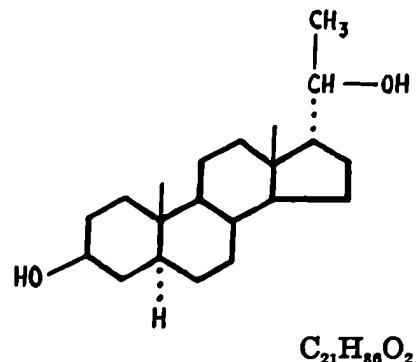
DERIVATIVES:

Diac. 168°: (1,2,5)

REFERENCES:

1. 78414
2. 70092
3. A17990
4. 72929
5. 73730
6. 80966
7. 76880
8. A17995

**17(α)-[1(β)-HYDROXYETHYL]-ANDROSTANE-3(β)-OL
(allo-pregnane-3(β),20(β)-diol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,5,6)

M.P.: 195-6°: (1)

194°: (5)

192-4°: (2,6)

PHARMACOLOGY:

Folliculoid: 55: inact.-R (4); 128C: 5 mg./day inact.-R (7).

Gonadotropic: 21: 10 mg. of diac. inact.-X (3).

Anesthetic: 11: U. > 20 mg.-R (4).

REMARKS:

DERIVATIVES:

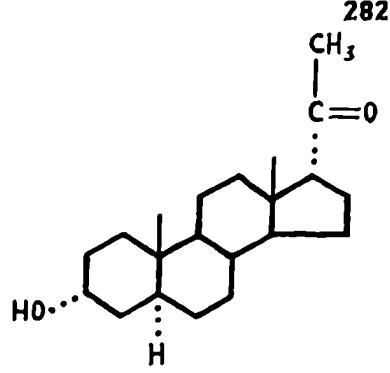
Diac. 142-3°: (1)

17¹-ac. 170-1°: (1)

REFERENCES:

1. A6243
2. 78114
3. 75731
4. A36744
5. 75131
6. 80968
7. A37486

**17(α)-[1-KETOETHYL]-ANDROSTANE-3(α)-OL
(*epi-allo-pregnanolone*)**



ISOLATION: Ur. (preg. human): (6)

STRUCTURE AND SYNTHESIS: (1,2,3,4,5,6,7,9)

M.P.: 170°: (1,3,7)

172-4°: (2)

$[\alpha]_D^{30} = +91^\circ$ (alc.): (6)

162-4°: (6)

173-4° (u): (5)

$[\alpha]_D = +87.7^\circ$ (alc.): (9)

176°: (4,9)

PHARMACOLOGY: Testoid: Test?: as act. as androsterone on s.ves.-R (1); **32A**: 2 mg. inact.-C (5); **63**: 300 γ /day inact.-C (5); **33**: 1-3 mg./day inact.-R (5).

REMARKS:

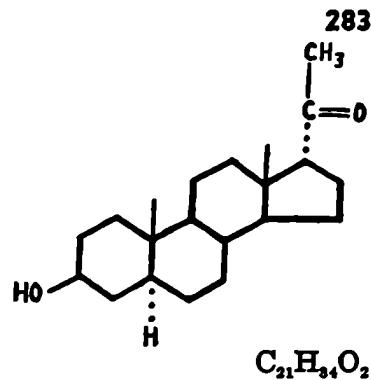
DERIVATIVES:

Ac. $\begin{cases} 141-2^\circ; [\alpha]^{22} = +94.5^\circ \text{ (alc.)}; (9) \\ 138-40^\circ; [\alpha]_D = 112^\circ \text{ (alc.)}; (2,5,6) \end{cases}$
Semicarb. 248-50°: (4,6)

REFERENCES:

1. 70101
2. 79639
3. 70097
4. 70095
5. 75053
6. A6244
7. 75181
8. S2124
9. A54963

17(α)-[1-KETOETHYL]-ANDROSTANE-3(β)-OL
(Luteosterone A, Wintersteiner's cpd. "A", allo-pregnanolone)



ISOLATION: Ad. (ox): (18)
 Ur. (preg. mare): (15,20)
 Ur. (preg. sow): (2)
 Ov. (sow): (4,7,8,9,12,23)
 Ur. (preg. human): (17,19)

STRUCTURE AND SYNTHESIS: (2,3,5,6,9,10,15,17)

M.P.: 194.5°(u): (1,5)
 193-4°: (2,6)
 195°: (10,15)
 194°: (4,9,12)
 190°: (7,8,17)

$[\alpha]_D^{10} = + 90.8^\circ$ (alc.): (1)
 $[\alpha]_D^{20} = + 70^\circ$ (alc.): (17)

PHARMACOLOGY:

Luteoid: **49**: up to 10 mg. inact.-Rb (12,24); **54**: 9.7 mg. inact.-Rb (7,8); **27**: up to 0.8 mg. inact.-G (13).

Folliculoid: **60**: act. of "allopregnanolone" < corresponding dione > diol-B (14); **55**: slight act.-R (10).

Anesthetic: **11**: U. = 12 mg.-R (16).

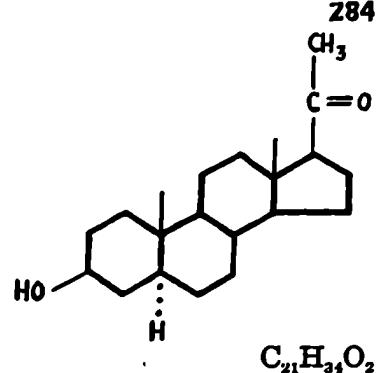
REMARKS: Ppt. with digitonin: (1,3)

DERIVATIVES:

Ac.	{ 144.5° (u): } $[\alpha]^{22} = + 79.8^\circ$ (alc.): (21)	(5,8,10,12)	1. 53438 2. 77851 3. 75053 4. 60177 5. 32394 6. 75181 7. 30175 8. 29808 9. 32391 10. 30540 11. 78851 12. 29442	13. A7023 14. A30007 15. A17988 16. A36744 17. 82703 18. 73504 19. 82124 20. A56072 21. A54003 22. 76733 23. 20044 24. 33809
Oxime	224.5° (u):	(5,12,17)		
Semicarb.	{ 249°: } 253°:	(7,8) (10)		
Ac-semicarb.	273°:	(10)		
17 ^o -Br.	144-5.5°:	(11)		
17 ^o -Cl.	157-9°:	(11)		
Phenylurethane	213-4.5°:	(7,8)		
p-nitrobz.	216°:	(7,8)		
Na sulfate ester ca.	193°:	(4)		
17 ^o -diazo	170-2°:	(22)		
3-ac.-17 ^o -diazo	134-4.5°:	(22)		

**17(β)-[1-KETOETHYL]-ANDROSTANE-3(β)-OL
(Iso-allo-pregnanolone)**

284



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 148° (u) : (1)

$[\alpha]_D^{10} = + 6.05^\circ$ (alc.) : (1)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin but ac. not ppt. (1).

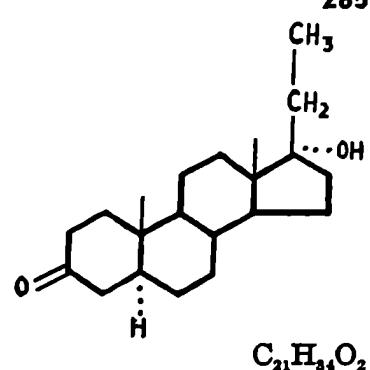
DERIVATIVES

Ac. 101° (u) : (1)

REFERENCES:

1. 53438

17(β)-ETHYL-ANDROSTANE-3-ONE-17(α)-OL
(Ethyl-dihydrotestosterone; 17-Ethyl-androstanolone)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 137-8°: (1)

PHARMACOLOGY:

Testoid: **29:** I.U. = 45-70 γ -C (5); **29:** U. = 20 γ ; slightly less act. than 17-me. cpd. or non-alkyl substituted ketol-C (2); **45:** s.ves. 100 γ inact., 29%/200 γ , 320%/500 γ ; pta. 100 γ inact., 28%/200 γ , 150%/500 γ -R (2.5).

Luteoid: **46:** + + +/20 mg.-Rb (3).

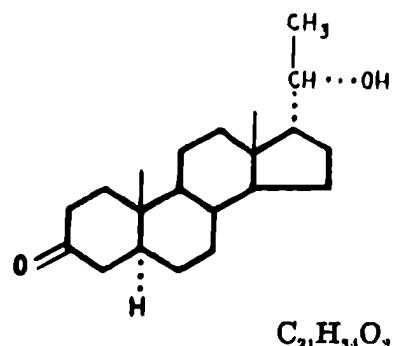
Gonadotropic: **21:** 20 mg. inact.-X (4).

REMARKS:

DERIVATIVES:

REFERENCES:

1. 54120
2. 56783
3. 67357
4. 75731
5. A33511

17(α)-[1(α)-HYDROXYETHYL]-ANDROSTANE-3-ONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)

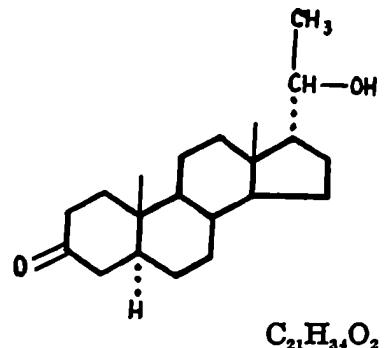
M.P.: 128°; (1)

PHARMACOLOGY:**REMARKS:****DERIVATIVES:**

3-ac. 117°; (1)

REFERENCES:

1. 70092

17(α)-[1(β)-HYDROXYETHYL]-ANDROSTANE-3-ONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1,2)**M.P.:** 195°: (1,2)**PHARMACOLOGY:****REMARKS:****DERIVATIVES:**

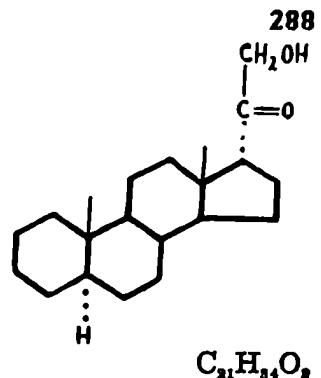
Ac. 156°: (1)

REFERENCES:

1. A6243
2. 70092

**17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE
[allo-pregnanol (21)-one (20)]**

288



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 115-7°: (1)

PHARMACOLOGY:

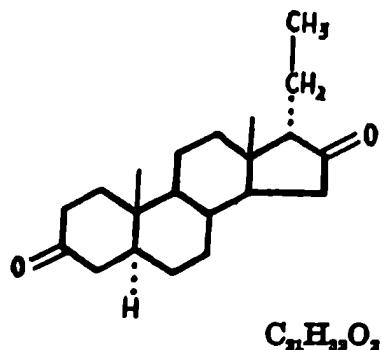
REMARKS:

DERIVATIVES:

Ac. 197-200°: (1)
Ac.-semicarb. 242-4°: (1)

REFERENCES:

1. 79003

17(α)-ETHYL-ANDROSTANE-3,16-DIONE**ISOLATION:****STRUCTURE AND SYNTHESIS:**

M.P.: 128°: (1)

PHARMACOLOGY:

REMARKS: Structure uncertain.

DERIVATIVES:

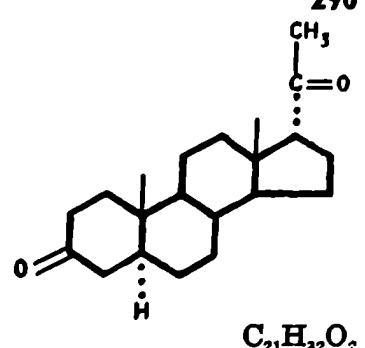
2:4-dinitrophenylhydrazone 245°: (1)

REFERENCES:

1. 75333

**17(α)-[1-KETOETHYL]-ANDROSTANE-3-ONE
(allo-pregnane-dione)**

290



ISOLATION: Ur. (preg. mare): (11)

STRUCTURE AND SYNTHESIS: (1,2,3,4,5,7,9,13,15,17)

M.P.: 200-2°:	(2,9)	$[\alpha]_D^{20} = + 126.9^\circ$ (alc.): (13)
200°:	(1,3)	
199°:	(4,6)	
200.5° (u):	(5,7,15)	
204-4.5°:	(17)	

PHARMACOLOGY:

Folliculoid: **60**: act. > than that of corresponding ketols or diols-B (10); **128C**: 8 mg. inact., 2-Br. cpd. act. questionable-R (15).

Gonadotropic: **21**: 5 mg. act.-X (12).

Anesthetic: **11**: 2-Br. cpd. inact.-R (16).

REMARKS: Ppt. by digitonin: (13)

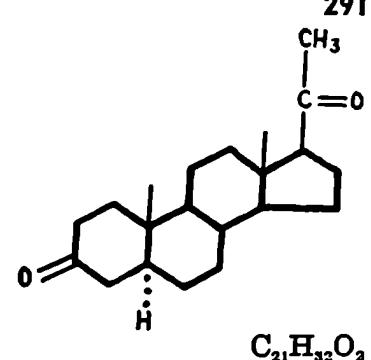
DERIVATIVES:

17 ² -Cl.	186-94°:	(8)
17 ² -Br.	177-9°:	(8)
2-Br.	199°:	(19)
Mono-semicarb.	245° (u):	(5)
Dioxime	260° (u):	(7)
Disemicarb.	> 325°:	(18)
2-pyridinium-br.	300-2°:	(20)

REFERENCES:

1. A6243
2. 72132
3. A6244
4. A17990
5. 55959
6. 72720
7. 29442
8. 78851
9. 81151
10. A30097
11. A17988
12. 75731
13. 53438
14. A38955
15. A37480
16. A38070
17. 31041
18. 70091
19. 53437
20. 75895

17(β)-[1-KETOETHYL]-ANDROSTANE-3-ONE
(Iso-allo-pregnane-dione)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 134-5° (u) : (1)
 148-9°: (2)

$[\alpha]_D^{20} = -14.6^\circ$ (alc.) : (1)

PHARMACOLOGY:

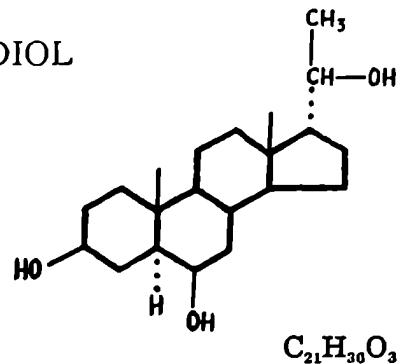
REMARKS: Not ppt. with digitonin: (1)

DERIVATIVES:

REFERENCES:

1. 53438
2. 75895

**17(α)-[1(β)HYDROXYETHYL]-ANDROSTANE-3(β),6(β)-DIOL
 (allo-pregnane-3(β),6(β),20(β)-triol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 222-4°: (1)
 224-6°: (2)

PHARMACOLOGY:

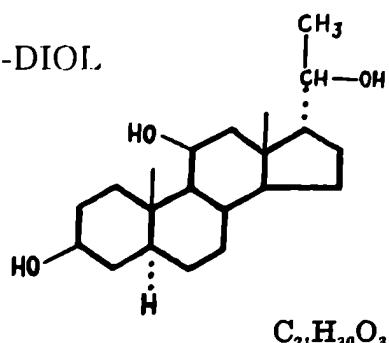
REMARKS:

DERIVATIVES:

Triac. 163-5°: (1)

REFERENCES:

1. 82783
2. 83068

17(α)-[1(β)-HYDROXYETHYL]-ANDROSTANE-3(β),11(β)-DIOL.**ISOLATION:****STRUCTURE AND SYNTHESIS:**

M.P.: 177-8°: (2)

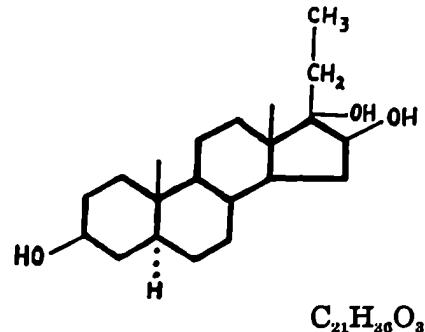
PHARMACOLOGY:

REMARKS: This structure was originally assigned to Reichstein's cpd. "J": (1); which is now known to be 17(α)-[1(β)-hydroxyethyl]-androstane-3(β),17(β)-diol. Mixture of 17¹ isomerides (2).

DERIVATIVES:**REFERENCES:**

1. A33510
2. 72132

**17()-ETHYL-ANDROSTANE-3(β),16(),17()-TRIOL
(allo-pregnane-3(β),16,17-triol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 240-1°: (1)

$[\alpha]_{D}^{21} = -28.5^\circ \pm 2^\circ$ (alc.): (1)

$[\alpha]_{5461}^{21} = -32.5^\circ \pm 3^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS: Structure uncertain (1)

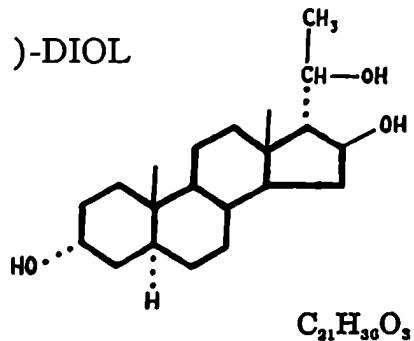
DERIVATIVES:

Diac. 160-1°; $\begin{cases} [\alpha]_D^{21} = -60.9^\circ \pm 2^\circ & (\text{acetone}): (1) \\ [\alpha]_{5461}^{21} = -74.5^\circ \pm 2^\circ & (\text{acetone}): (1) \end{cases}$

REFERENCES:

1. 78849

**17(α)-[1(β)-HYDROXYETHYL]-ANDROSTANE-3(α),16(β)-DIOL
(Pregnanetriol "B")**



ISOLATION: Ur. (preg. mare): (1,4,5,6,7)

STRUCTURE AND SYNTHESIS: (2,3,6,7)

M.P.: 300°: (6)
300-2°: (7)

$[\alpha]_{D461} = -44^\circ$ (pyridine) : (6)
 $[\alpha]_D = -41^\circ$ (pyridine) : (7)

PHARMACOLOGY:

REMARKS:

Considered at first to be 3(α),4(β),20(α)-pregnanetriol (2); the 3 α ,6,20-pregnane-or allo-pregnane-triol structure suggested tentatively (5); later, on revised evidence, considered to be a 3 α ,16,20 "allo"-triol (3).

Not ppt. with digitonin (7).

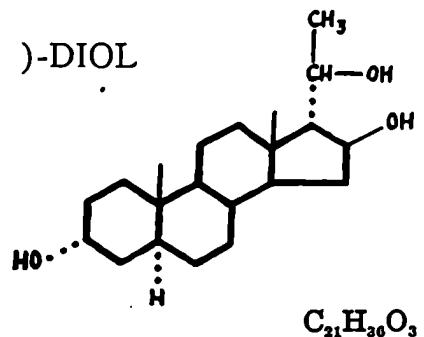
DERIVATIVES:

17 ¹ -monoac.	233-5°: (3)
Triac.	168°: (2,3,5)
Tribz.	218°: (2)
Monoac.	222-4°: (5)

REFERENCES:

1. 75258
2. 72020
3. 75333
4. 29046
5. 73563
6. 14766
7. 71510

**17(α)-[1(β)-HYDROXYETHYL]-ANDROSTANE-3(α),16(β)-DIOL
 (allo-pregnane-3(α),16,20-triol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 210-2: (1)

PHARMACOLOGY:

REMARKS:

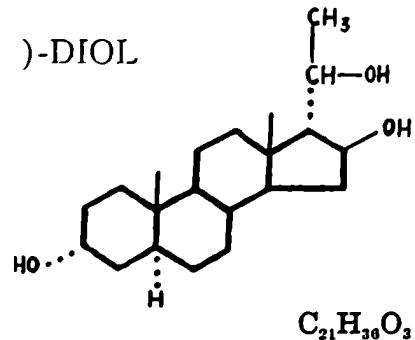
DERIVATIVES:

Triac. 148-50° : (1)

REFERENCES:

I. 80965

**17(α)-[1(β)-HYDROXYETHYL]-ANDROSTANE-3(α),16(β)-DIOL
(allo-pregnane-triol-3 α ,16,20 β)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 263-5°: (1)

PHARMACOLOGY:

REMARKS:

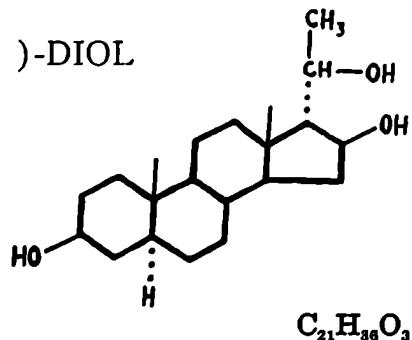
DERIVATIVES:

Triac. 181°: (1)

REFERENCES:

- 1. 80968

**17(α)-[1(β)-HYDROXYETHYL]- ANDROSTANE-3(β),16(β)-DIOL
 (allo-pregnane-3,16,20-triol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 285-8°: (1,2)

PHARMACOLOGY:

REMARKS:

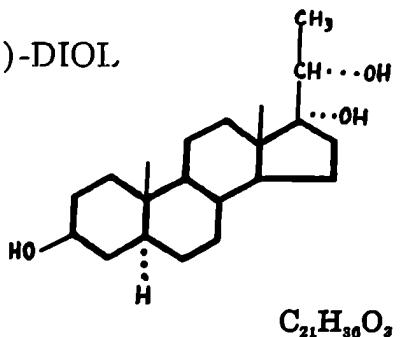
DERIVATIVES:

Triac. 161-3°: (1)

REFERENCES:

1. 80966
2. 80968

**17(β)-[1(α)-HYDROXYETHYL]- ANDROSTANE-3(β),17(α)-DIOL
(allo-pregnane-3(β),17(α),20(α)-triol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 212-4°: (1,2)
202-15°: (2)

$[\alpha]_D = -16.7^\circ \pm 2^\circ$ (alc.): (1,2)
 $[\alpha]_{5461}^{21} = -18.7^\circ \pm 2^\circ$ (alc.): (2)

PHARMACOLOGY:

REMARKS:

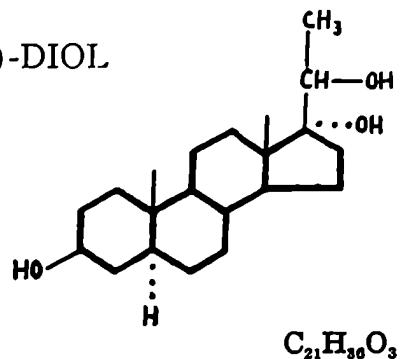
DERIVATIVES:

Diac. 135-6°; $\begin{cases} [\alpha]_D = -18.2^\circ \pm 1^\circ \text{ (acetone)} : (1,2) \\ [\alpha]_D = -21.8^\circ \pm 1^\circ \text{ (acetone)} : (2) \end{cases}$

REFERENCES:

1. 81147
2. 78849

**17(β)-[1(β)-HYDROXYETHYL]-ANDROSTANE-3(β),17(α)-DIOL
(allo-pregnane-3(β),17(α),20(β)-triol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 234°: (1)

$[\alpha]_D = -8.7^\circ \pm 1.8^\circ$ (alc.): (1)
 $[\alpha]_{6461}^{21} = -11.6^\circ \pm 1.8^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS:

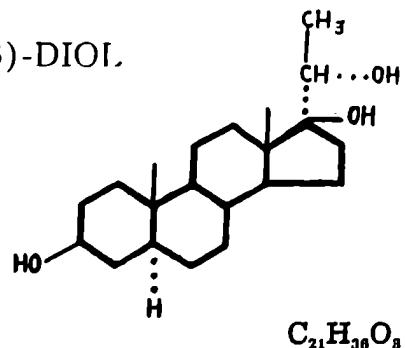
DERIVATIVES:

Diac. 202°; $[\alpha]_D = -10.9^\circ$ (CHCl_3): (1)

REFERENCES:

1. 81147

**17(α)-[1(α)-HYDROXYETHYL]-ANDROSTANE-3(β),17(β)-DIOL
(Reichstein's cpd. "O")**



ISOLATION: Ad. (2)

STRUCTURE AND SYNTHESIS: (1,2,3,4)

M.P.: 221-2°: (1,2,3)

$[\alpha]_D^{20} = -12.5^\circ \pm 2^\circ$ (Me.-alc.): (1,2,3)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin (2).

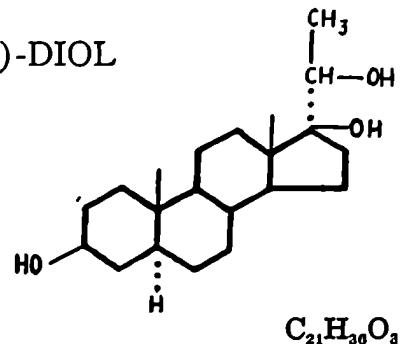
DERIVATIVES:

Diac. { 250-2°; $[\alpha]_D = -30^\circ$ (acetone): (1,2,3,5)
 { 249-50°; $[\alpha]_D = -33^\circ$ (acetone): (4)

REFERENCES:

1. 81147
2. 72131
3. 78349
4. 81149
5. 81790

**17(α)-[1(β)-HYDROXYETHYL]- ANDROSTANE-3(β),17(β)-DIOL
(Reichstein's cpd. "J"; allo-pregnane-3(β),17(β),20(β)-triol)**



ISOLATION: Ad. (2,6,7)

STRUCTURE AND SYNTHESIS: (1,2,3,4,5,6)

M.P.: 216-7°: (6)

206-12°: (2)

230°: (1,3)

$[\alpha]_D^{20} = -8^\circ \pm 1^\circ$ (alc.): (2,3)

PHARMACOLOGY: Corticoid: **52**: Dose? inact.-R (7)

Gonadotropic: **21**: 6 mg. act.-X (9)

Anesthetic: **11**: 30 mg. inact.-R (8)

REMARKS:

DERIVATIVES:

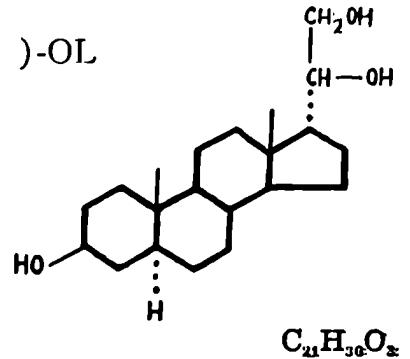
Diac. $\begin{cases} 161-2^\circ; [\alpha]_D = +27^\circ \text{ (acetone)} : (1,2,3,5) \\ 159-61^\circ; [\alpha]_D = +24^\circ \text{ (acetone)} : (4) \end{cases}$

REFERENCES:

1. 81147
2. 72131
3. 78849
4. 81140
5. 81790
6. 63690
7. A9075
8. A36744
9. 75731

**17(α)-[1(),2()-DIHYDROXYETHYL]-ANDROSTANE-3()-OL
(allo-pregnane-3(),20(),21()-triol)**

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ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 219°: (1)

PHARMACOLOGY:

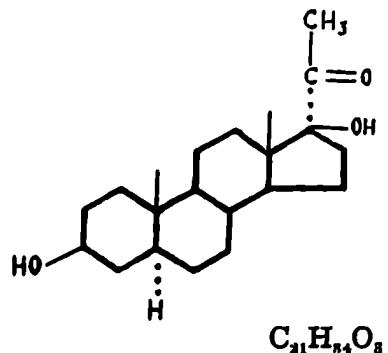
REMARKS:

DERIVATIVES:

REFERENCES:

1. 72132

17(α)-[1-KETOETHYL]-ANDROSTANE-3(β),17(β)-DIOL
 (Reichstein's cpd. "L"; Wintersteiner's cpd. "G";
 allo-pregnane-3(β),17(β)-diol-20-one)



ISOLATION: Ad. (1,2,3)

STRUCTURE AND SYNTHESIS: (2,3,6,8)

M.P.: 272°: (2)

264-6°: (2)

264°: (4)

$[\alpha]_D^{20} = +38^\circ \pm 1^\circ$ (alc.): (4)

$[\alpha]_D^{21} = +30.6^\circ \pm 3^\circ$ (alc.): (2)

PHARMACOLOGY: Corticoid: 56: 50γ/kg./day inact.-D (4)

Folliculoid: 55: 5 mg. of diac. questionably act.-R (9).

Anesthetic: 11: 10 mg. of 3-ac. inact.-R (5)

REMARKS:

DERIVATIVES:

3-ac. { 191-2°:
 189-90°; $[\alpha]_D^{18} = +15.2^\circ \pm 3^\circ$ (acetone): (3,6,7)

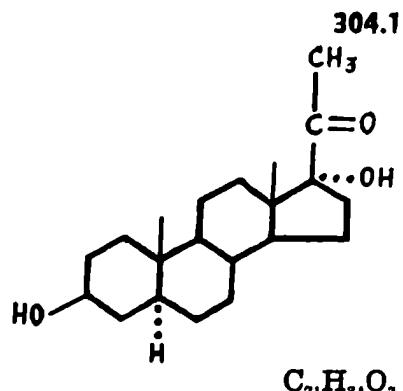
Semicarb. 263-5°: (4)

Diac. 172°: (9)

REFERENCES:

1. 63890
2. 73593
3. A19374
4. A1688
5. A36744
6. 81150
7. 81790
8. 81695
9. A37486

17(β)-[1-KETOETHYL]-ANDROSTANE-3(β),17(α)-DIOL



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3,4)

M.P.:

PHARMACOLOGY:

REMARKS: The ac. and diac. had previously been regarded as derivatives of cpd. 530 (1,2,3), but this has been shown to be incorrect (4).

DERIVATIVES:

Diac. $227\text{-}9^\circ$; $[\alpha]_D^{18} = 0^\circ \pm 2^\circ$ (dioxane) :

(1,2,3,4) 1. 75155

17-ac. $202\text{-}4^\circ$; $[\alpha]_D = 0^\circ$ (dioxane) :

(3,4) 2. 73580

3-ac. $181\text{-}3^\circ$ and $192\text{-}4^\circ$; $[\alpha]_D^{21} = -24.3^\circ \pm 3^\circ$; $[\alpha]_{5461}^{23} = -29.4^\circ \pm 3^\circ$ (dioxane) :

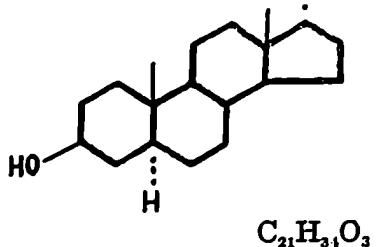
(4) 3. 75679

4. 84189

REFERENCES:

**17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(β)-OL
(allo-pregnane-diol-3(β),21-one-20)**

305



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.:

PHARMACOLOGY:

REMARKS:

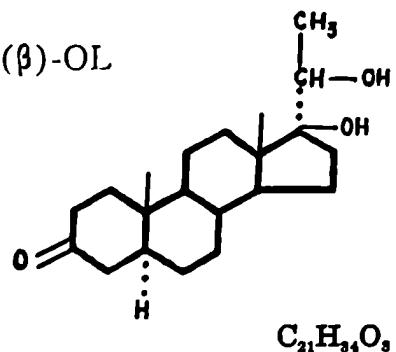
DERIVATIVES:

Diac. $153\text{-}4^\circ$ $\left\{ [\alpha]_{D}^{17} = +77^\circ \text{ (acetone)}; [\alpha]_{D}^{17} = +93^\circ \text{ (acetone)} : (3) \right.$
 $\left. [\alpha]_{D}^{10} = +78^\circ \text{ (dioxane)}; [\alpha]_{D}^{10} = +94.4^\circ \text{ (dioxane)} : (3) \right.$
 152-3.5°: (1,2)
 17²-ac. 202-4°: (2)

REFERENCES:

1. 76735
2. 76733
3. 83506

**17(α)-[1(β)-HYDROXYETHYL]- ANDROSTANE-3-ONE-17(β)-OL
(allo-pregnane-3-one-17(β),20(β)-diol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 170° + 181-2°: (1)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

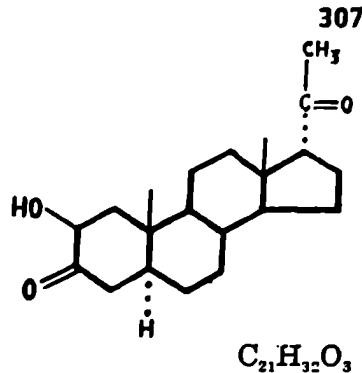
Ac. 189-90°; $[\alpha]_D^{18} = + 48.7^\circ$ (acetone): (1)

REFERENCES:

1. 81702

**17(α)-[1-KETOETHYL]-ANDROSTANE-2(β)-OL-3-ONE
(allo-pregnane-2-ol-3,20-dione)**

307



ISOLATION:

STRUCTURE AND SYNTHESIS:

M.P.:

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

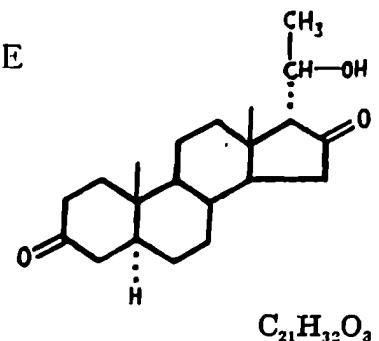
Bz. 235° : (1)

REFERENCES:

1. 53437

**17(α)-[1(β)-HYDROXYETHYL]-ANDROSTANE-3,16-DIONE
(allo-pregnane-3,16-dione-20-ol)**

308



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS: Structure uncertain (1)

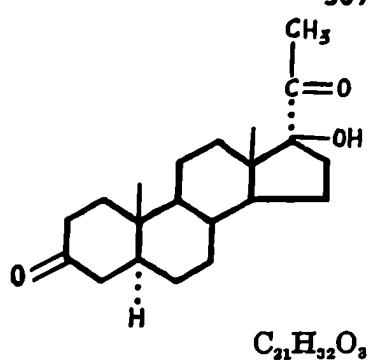
DERIVATIVES:

Ac. 191°: (1)

REFERENCES:

1. 75333

**17(α)-[1-KETOETHYL]-ANDROSTANE-3-ONE-17(β)-OL
 (allo-pregnane-3,20-dione-17(β)-ol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 270-2°: (1)

PHARMACOLOGY:

REMARKS:

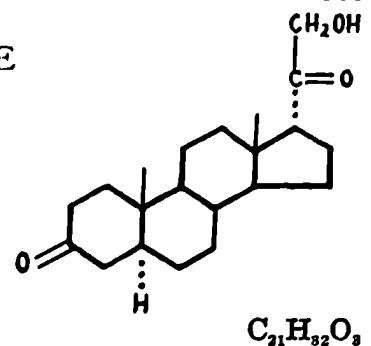
DERIVATIVES:

REFERENCES:

1. 73593

**17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3-ONE
(allo-pregnane-3,20-dione-21-ol)**

310



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY: Corticoid: 53A: ac. inact. at 2 mg./day-R (2)

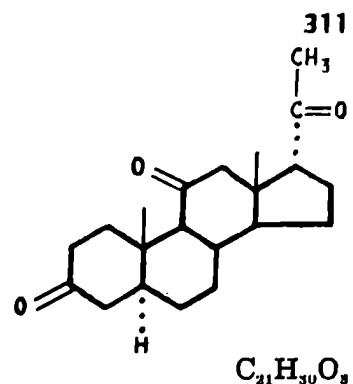
REMARKS:

DERIVATIVES:

Ac. 197-9°; $[\alpha]_D = +115^\circ \pm 2^\circ$ (CHCl_3): (1,2)
Dioxime-ac. 212-4°: (2)

REFERENCES:

1. 76733
2. 79622

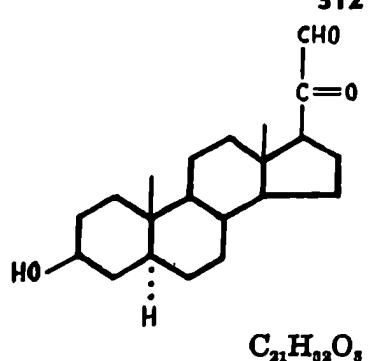
17(α)-[1-KETOETHYL]-ANDROSTANE-3,11-DIONE**ISOLATION:****STRUCTURE AND SYNTHESIS:** (1)

M.P.: 212-6°: (1)

 $[\alpha]_D^{20} = +133^\circ \pm 2^\circ$ (alc.): (1)**PHARMACOLOGY:****REMARKS:****DERIVATIVES:****REFERENCES:**

1. 72132

**17()-[1-KETO-2-ALDOETHYL]-ANDROSTANE-3(β)-OL.
(testololone, cpd. "A")**



ISOLATION: Te.: (1,2)

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 258-64°: (1,2)

$[\alpha]_D^{24} = - 67.4^\circ$ (pyridine): (1,2)

PHARMACOLOGY: Testoid: Test?: "no androgenic act.-Species? (1,2)

REMARKS: Steric configuration at C₆ uncertain (2).

DERIVATIVES:

Mono-bz.	218-24°: (1,2)
Bz.-semicarb.	226-35.5°: (1,2)
Dioxime	234-5°: (1,2)
Ac.-dioxime	153-4°: (1,2)
Semicarb.	237.5-8.5°: (1,2)
Digitonide	250°: (1,2)

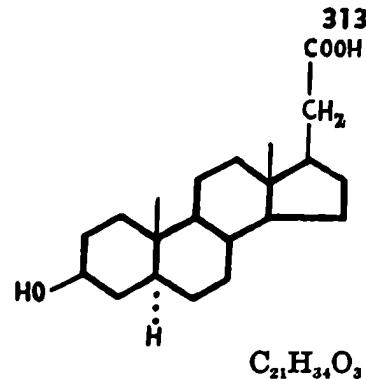
REFERENCES:

1. A54248
2. A58831

**17()-CARBOXYMETHYL-ANDROSTANE-3(β)-OL
(allo-pregnane-3(β)-ol-acid-21)**

313

C₂₀H₃₂O₃



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 228-30°: (1)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

Ac. 191-3°: (1)
Ac.-me. ester 150-1°; $[\alpha]_D = 0^\circ$: (2)

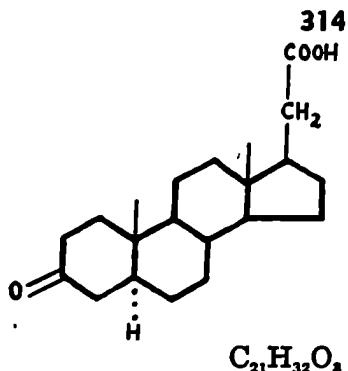
REFERENCES:

1. 83173
2. 77141

17()-CARBOXYMETHYL-ANDROSTANE-3-ONE
(3-keto-allo-pregnanoic acid-21)

314

COOH



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

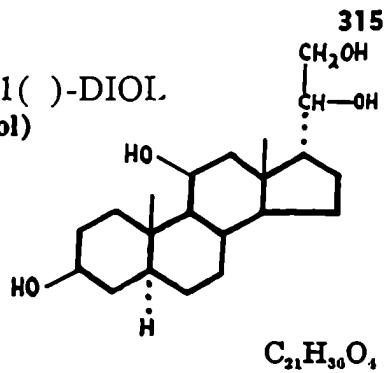
DERIVATIVES:

Me. ester 139-40° : (1)

REFERENCES:

1. 81791

**17(α)-[1(β),2-DIHYDROXYETHYL]-ANDROSTANE-3(β),11(β)-DIOIL
(Kendall's hexahydro cpd. "B"; allo-pregnane-3(β),11(β),20(β),21-tetrol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 215-8°: (1)
220-2.5° (u): (2)

$[\alpha]_{D}^{23} = + 39.2^\circ \pm 4^\circ$ (alc.): (2)

PHARMACOLOGY:

REMARKS:

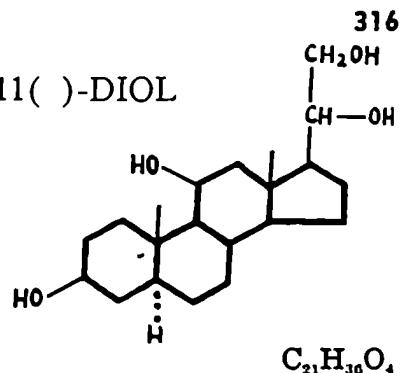
DERIVATIVES:

REFERENCES:

I 72132

17()-[1(),2-DIHYDROXYETHYL]-ANDROSTANE-3(β),11()-DIOL
(*allo-pregnane-tetrol-3(β),11,20,21)*

316



ISOLATION: Ur. (Stallion): (1)

STRUCTURE AND SYNTHESIS: (1)

M.P.: 295°: (1)

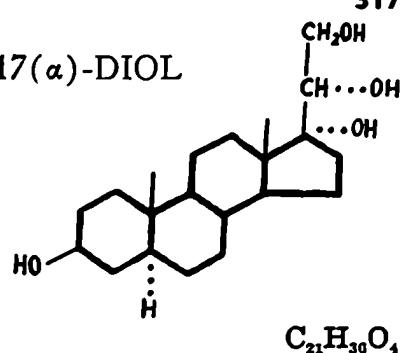
PHARMACOLOGY:

REMARKS: Structure very uncertain (1). Ppt. with digitonin (1).

DERIVATIVES

REFERENCES:

17(β)-[1(α),2-DIHYDROXYETHYL]-ANDROSTANE-3(β),17(α)-DIOL
 (allo-pregnane-tetrol-3(β),17(α),20(α),21)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 236°: (3)

$[\alpha]_D = 0^\circ$ (alc.): (3)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

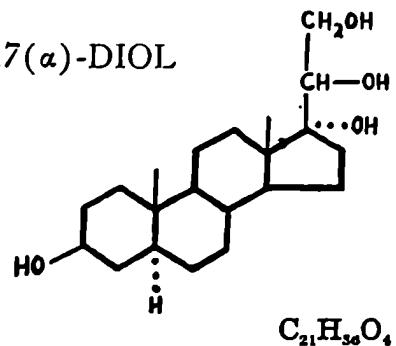
3,17¹,17²-triac. 119-21°; $\left\{ \begin{array}{l} [\alpha]_{D}^{15} = -31.5^\circ \text{ (acetone)} : (1,2,3,4) \\ [\alpha]_{5461}^{15} = -38.5^\circ \text{ (acetone)} : (1,2,3,4) \end{array} \right.$

REFERENCES:

1. 81606
2. A35088
3. 81147
4. 83470

**17(β)-[1(β),2-DIHYDROXYETHYL]-ANDROSTANE-3(β),17(α)-DIOL
(allo-pregnane-3(β),17(α),20(β),21-tetrol)**

318



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 210°: (3)

$[\alpha]_D^{20} = 0^\circ$ (alc.): (2)

PHARMACOLOGY:

REMARKS:

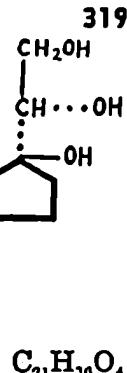
DERIVATIVES:

3,17¹,17²-triac. {146-8°; $[\alpha]_D^{20} = 0^\circ$ (acetone): (1,2)
150°: (3)}

REFERENCES:

1. 81606
2. A35088
3. 81147

**17(α)-[1(α),2-DIHYDROXYETHYL]- ANDROSTANE-3(β),17(β)-DIOL
(allo-pregnane-3(β),17(β),20(α),21-tetrol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3,4)

M.P.: 283-6°: (1,2)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin (1).

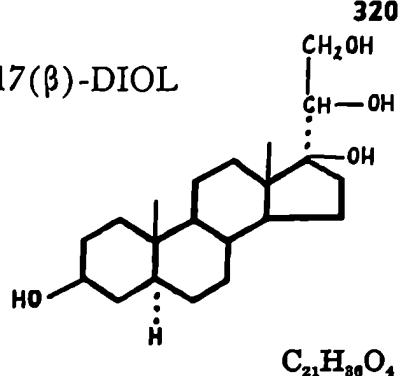
DERIVATIVES:

3,17 β ,17 α -triacet. (178°; $[\alpha]_{D}^{25} = -1.3^\circ \pm 2^\circ$ (acetone); (3)
(180-1; $[\alpha]_D = 0^\circ$ (acetone); (1,2)

REFERENCES:

- 1 A10373
- 2 81147
- 3 81701
- 4 A35088

**17(α)-[1(β),2-DIHYDROXYETHYL]-ANDROSTANE-3(β),17(β)-DIOL
(Reichstein's cpd. "K"; allo-pregnane-3(β),17(β),20(β),21-tetrol)**



ISOLATION: Ad. (1)

STRUCTURE AND SYNTHESIS: (1,2,3,4,5,7)

M.P.: 198-200°: (1,5)

$$\left\{ \begin{array}{l} [\alpha]_D = 0^\circ \text{ (alc.) : } (5) \\ [\alpha]_D^{21} = -1^\circ \pm 2^\circ \text{ (alc.) : (1)} \end{array} \right.$$

PHARMACOLOGY: Corticoid: "Inactive in all bioassay methods used"- (8).

REMARKS: Ppt. with digitonin (1)

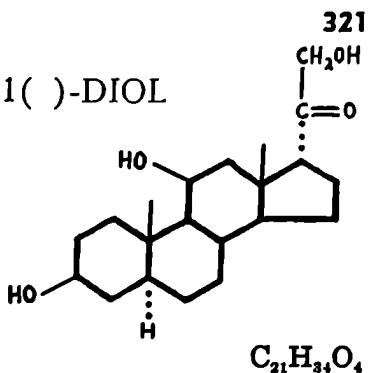
DERIVATIVES:

3,17¹,17²-triac. 179-80°; $[\alpha]_D^{20} = +57^\circ \pm 3^\circ$ (acetone): (1,3,5,6)

REFERENCES:

1. 72131
2. A9625
3. A10373
4. 75154
5. 81147
6. 81791
7. A35088
8. A58412

17(α)-[1-KETO-2-HYDROXYETHYL]- ANDROSTANE-3(β),11()-DIOL
 (Reichstein's cpd. "R"; allo-pregnane-3(β),11,21-triol-20-one)



ISOLATION: Ad. (1)

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 202-4°: (1,2)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

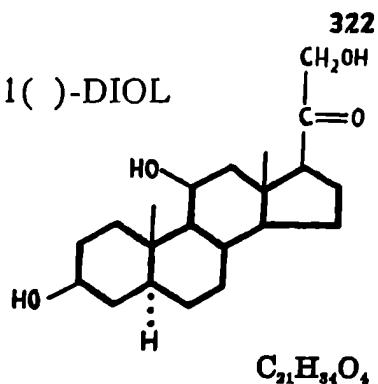
3,17²-diac. 173-4°; $\left\{ [\alpha]_D^{17} = +83.7^\circ \pm 2^\circ; [\alpha]_{5461}^{17} = +102.7^\circ \pm 2^\circ \text{ (dioxane)} : (3) \right.$

1. A19374
2. 73592
3. 83506

REFERENCES:

17(β)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(β),11()-DIOL
(Reichstein's cpd. "Iso-R"; iso-allo-pregnane-3(β),11,21-triol-20-one)

322



ISOLATION:

STRUCTURE AND SYNTHESIS:

M.P.:

PHARMACOLOGY:

REMARKS:

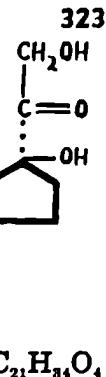
DERIVATIVES

3,17²-diac. 147-8°; $[\alpha]_D^{18} = -60^\circ \pm 1.5$ (acetone); (1)

REFERENCES:

1. 78846

17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(β),17(β)-DIOL
 (Reichstein's cpd. "P"; allo-pregnane-3(β),17(β),21-triol-20-one)



ISOLATION: Ad. (1)

STRUCTURE AND SYNTHESIS: (1,3,4,5)

M.P.: 230-9°: (1)

$[\alpha]_D^{20} = +48^\circ \pm 3^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin: (1)

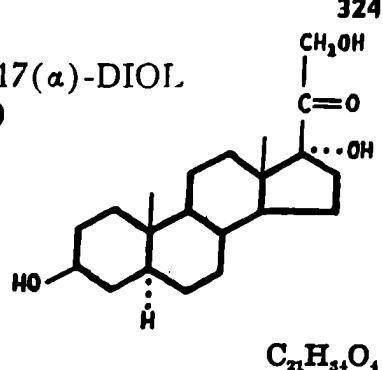
DERIVATIVES:

Triac.	190-2° (not quite pure):	(2)
	$211-2^\circ$; $[\alpha]_{D}^{12} = +46^\circ \pm 2^\circ$ (CHCl_3):	(1,4)
3,17 ² -diac.	$\left\{ \begin{array}{l} 208-9^\circ; [\alpha]_{D}^{18} = +44.5^\circ \pm 3^\circ \text{ (dioxane)}: \\ [\alpha]_{5461}^{18} = +57.4^\circ \pm 3^\circ \text{ (dioxane)}: \end{array} \right.$	(6)

REFERENCES:

1. A19373
2. 76735
3. 75154
4. 81152
5. 75747
6. 83506

17(β)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(β),17(α)-DIOL
(Reichstein's cpd. "Iso-P"; iso-allo-pregnane-3(β),17(α)-21-triol-20-one)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.:

PHARMACOLOGY:

REMARKS: Free cpd. not obtained in pure form: (2)

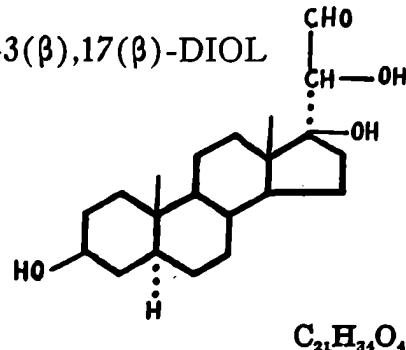
DERIVATIVES:

3,17²-diac. 159-61°; $\left\{ \begin{array}{l} [\alpha]_D = -2900^\circ \text{ (dioxane)} : (3) \\ [\alpha]_D^{10} = -68^\circ \pm 4^\circ; \quad [\alpha]_{5461}^{10} = -89.7^\circ \pm 4^\circ \text{ (dioxane)} : (1) \\ [\alpha]_D^{10} = -55.7^\circ \pm 2^\circ; \quad [\alpha]_{5461}^{10} = -66.5^\circ \pm 2^\circ \text{ (acetone)} : (2) \end{array} \right.$
 Triac. 179-81°; $[\alpha]_D^{10} = -12.8^\circ \pm 5^\circ; \quad [\alpha]_{5461}^{10} = -18.9^\circ \pm 5^\circ \text{ (acetone)} : (2)$
 3-ac. 195-7°; $[\alpha]_D^{10} = -43^\circ \pm 3^\circ \text{ (acetone)} : (2)$

REFERENCES:

1. 83506
2. 83470
3. A58412

**17(α)-[1(β)-HYDROXY-2-ALDOETHYL]-ANDROSTANE-3(β),17(β)-DIOL
(allo-pregnane-3(β),17(β),20(β)-triol-21-al)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 185-202° (crude): (1)

PHARMACOLOGY:

REMARKS:

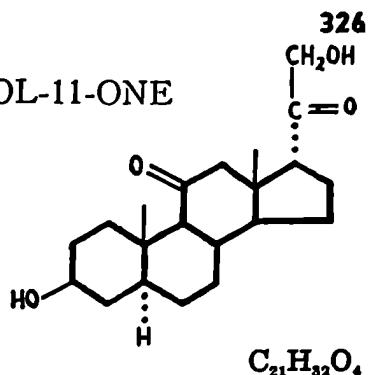
DERIVATIVES:

3,17¹-diac. 181-3°; $[\alpha]_D^{10} = +36^\circ \pm 2^\circ$ (dioxane): (1) 1. 81152

REFERENCES:

17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(β)-OL-11-ONE

(Kendall's cpd. "H"; Reichstein's cpd. "N"; allo-pregnane-3(β),21-diol-11,20-dione)



ISOLATION: Ad. (1,2,4)

STRUCTURE AND SYNTHESIS: (1,3)

M.P.: 189-91°: (2)
172-6° (u): (1)

$[\alpha]_D^{19} = + 93.8^\circ \pm 2^\circ$ (alc.) : (2)
 $[\alpha]_{5461}^{25} = + 118^\circ$ (alc.) : (1)

PHARMACOLOGY:

Corticoid: 47: “ α , β unsaturated ketone group essential for physiol. act.”-R (1); Test? inact. (7).

Luteoid: 46: 20 mg. of impure cpd. inact.-Rb. (9).

Anesthetic: 11: U. = 7 mg. of impure cpd.-R (6); 127: inact. up to 3.0 mg. fish (8).

REMARKS: Ppt. with digitonin: (1)

DERIVATIVES:

Diac. $\begin{cases} 148-9.5^\circ; & \left\{ \begin{array}{l} [\alpha]_D^{18} = + 77.5^\circ \pm 2.5^\circ \text{ (acetone)} : (5) \\ [\alpha]_{5461}^{18} = + 99.5^\circ \pm 2.5^\circ \text{ (acetone)} : (5) \end{array} \right. \\ 144-5^\circ; & \left\{ \begin{array}{l} [\alpha]_D^{19} = + 85.6^\circ \text{ (dioxane)} : (10) \\ [\alpha]_{5461}^{19} = + 105.6^\circ \text{ (dioxane)} : (10) \end{array} \right. \end{cases}$

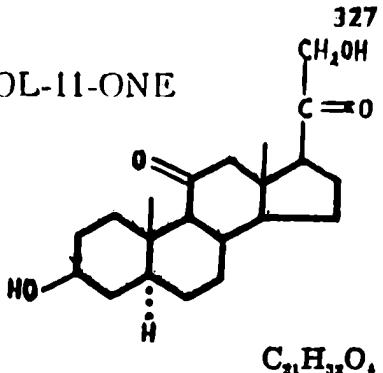
REFERENCES:

1. 60294
2. 72131
3. A19373
4. A19374
5. 78846
6. A36744
7. Kendall (personal communication)
8. A38070
9. A56335
10. 83506

17(β)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(β)-OL-11-ONE

(Reichstein's cpd. "17-keto-N"; Iso-allo-
pregnane-3(β),21-diol-11,20-dione)

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ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

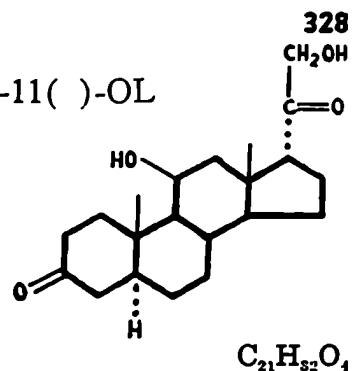
Diac. 131-2°; $[\alpha]_D^{24} = -44^\circ \pm 3^\circ$ (acetone): (1)

REFERENCES:

1. 78846

17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3-ONE-11(β)-OL
(Kendall's dihydro cpd. "B"; dihydrocorticosterone;
allo-pregnane-3,20-dione-11,21-diol)

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ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 184-7° (u) : (1)

[α]_D²⁵ = + 157° (alc.) : (1)

PHARMACOLOGY: Corticoid: 47A: 10 mg./day as act. as 0.2 mg. of corticosterone-R (1).

REMARKS:

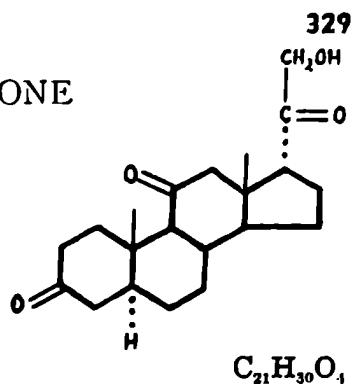
DERIVATIVES:

REFERENCES:

1. 69204

17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3,11-DIONE
(Kendall's dihydro cpd. "A"; allo-pregnane-3,11,20-trione-21-ol)

329



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 174-6° (u): (1)

$[\alpha]_{\text{D}461}^{25} = +163^\circ$ (alc.): (1)

PHARMACOLOGY:

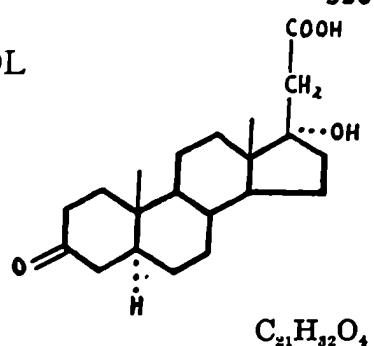
REMARKS:

DERIVATIVES:

REFERENCES:

1. 69294

17(β)-[CARBOXYMETHYL]-ANDROSTANE-3-ONE-17(α)-OL
 [androstane-ol(17 α)-one-(3)-acetic acid-(17)]



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

Me. ester 179-81°: (1)

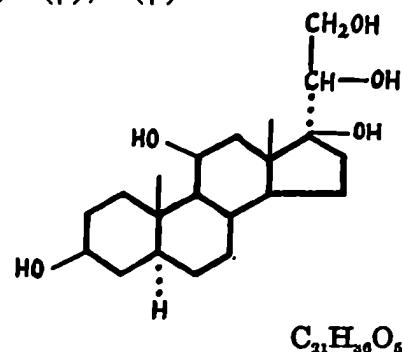
REFERENCES:

1. 75152

17(α)-[1(),2-DIHYDROXYETHYL]-ANDROSTANE-3(β),11(β),17(β)-TRIOL

(Wintersteiner's cpd. "A"; Reichstein's cpd. "A"; Kendall's
cpd. "D"; allo-pregnane-3(β),11(β),17(β),20,21-pentol)

ISOLATION: Ad.: (1,2,3,6,10)



STRUCTURE AND SYNTHESIS: (1,4,5,7,11,12)

M.P.: 213-4° (u): (1)
214-6° (u): (2,8)
222-4°: (3,9)
165-7°: (4)

$[\alpha]_D^{19} = +16^\circ \pm 1^\circ$ (alc.): (3)

$[\alpha]_{5461}^{25} = +29^\circ$ (acetone): (2)

PHARMACOLOGY: Corticoid: 61: 40γ/kg./day inact.-D (1); 52: Dose? inact.-R (3).

REMARKS: (2,3) suggest that lower M.P. (4) is due to hydration. Ppt. with digitonin (5,8)

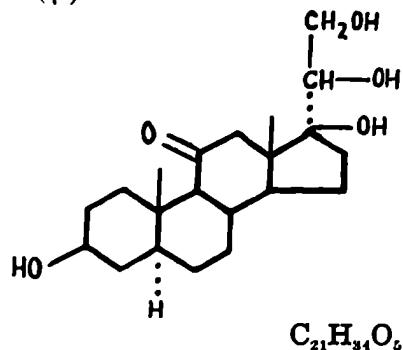
DERIVATIVES:

3,17¹,17²-triac. 219-20°; $[\alpha]_D^{19} = +74^\circ \pm 2^\circ$ (acetone): (8,10)
Monoacetone cpd. 209-10°: (9)
Tetra-or penta-ac. 150-1°: (9)

REFERENCES:

1. 53072
2. 60490
3. 34011
4. 72169
5. 63602
6. 63600
7. 78847
8. 78846
9. A33510
10. 83407
11. 83506
12. A58412

**17(α)-[1(β),2-DIHYDROXYETHYL]-ANDROSTANE-3(β),17(β)-DIOL-11-ONE
 (allo-pregnane-3(β),17(β),20,21-tetrol-11-one)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 160-70° + 212-6°: (1)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin (1)

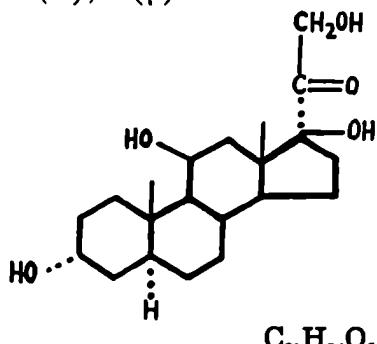
DERIVATIVES:

3,17¹,17²-triac. 183-4° + 211-2°; $[\alpha]_D^{14} = + 69^\circ \pm 3.5^\circ$ (acetone): (1)

REFERENCES:

1. 78846

**17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(α),11(),17(β)-TRIOL
 (Kendall's cpd. "C"; Reichstein's cpd. "C"; Wintersteiner's cpd. "D";
 allo-pregnane-3(α),11,17(β),21-tetrol-20-one)**



ISOLATION: Ad.: (1,2,3,4,5,6,8,11)

STRUCTURE AND SYNTHESIS: (4,7,10,11)

M.P.: 273-6°: (11) $[\alpha]_{D}^{18} = +59.2^\circ \pm 5^\circ$ (dioxane); $[\alpha]_{D}^{18} = +75.7^\circ \pm 5^\circ$ (dioxane): (11)
 250-3° (u): (4) $[\alpha]_{D}^{15} = +73^\circ \pm 4^\circ$ (alc.); $[\alpha]_{D}^{15} = +90^\circ \pm 4^\circ$ (alc.): (11)
 253-6°: (3) $[\alpha]_{D}^{20} = +69.8^\circ \pm 2.5^\circ$ (alc.): (3)
 $[\alpha]_{D}^{25} = +84.2^\circ \pm 5.3^\circ$ (alc.): (4)

PHARMACOLOGY: Corticoid: **52**: Dose? inact.-R (3); **61**: 20 γ /kg./day inact.-D (5); **79**: U. = $\frac{1}{4}$ -
 $\frac{1}{3}$ mg.-R (8)

REMARKS: Not ppt. with digitonin (11).

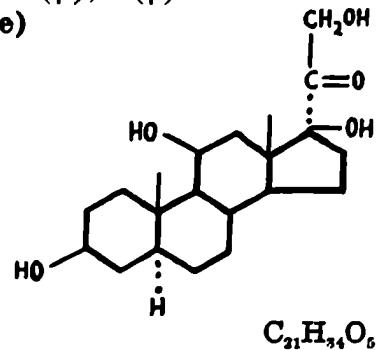
DERIVATIVES:

3,17 α -diac. 204-6°; $[\alpha]_{D}^{15} = +73.8^\circ$; $[\alpha]_{D}^{15} = +90.5^\circ$ (dioxane): (9,11)
 Semicarb. 243-5°: (3)

REFERENCES:

1. 31645
2. 68081
3. 34911
4. 72160
5. 53072
6. 60190
7. 63692
8. A30091
9. A9076
10. A33510
11. 83506

**17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(β),11(β),17(β)-TRIOL
(Reichstein's cpd. "V"; allo-pregnane-3(β),11(β),17(β),21-tetrol-20-one)**



ISOLATION: Ad.: (1)

STRUCTURE AND SYNTHESIS: (1)

M.P.: 220-5°: (1)

$[\alpha]_D^{13} = +50.7^\circ \pm 3^\circ$ (dioxane): (1)
 $[\alpha]_{5461}^{13} = +68^\circ \pm 3^\circ$ (dioxane): (1)

PHARMACOLOGY:

REMARKS: Ppt. with digitonin (1)

DERIVATIVES:

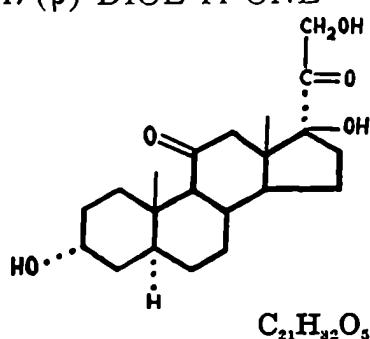
3,17²-diac. 225-7°; $\begin{cases} [\alpha]_D^{18} = +62.6^\circ \pm 2^\circ & \text{(dioxane): (1)} \\ [\alpha]_{5461}^{17} = +77.3^\circ \pm 2^\circ & \text{(dioxane): (1)} \end{cases}$

REFERENCES:

1. 83506

**17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(α),17(β)-DIOL-11-ONE
 [allo-pregnane-triol-(3 α ,17 β ,21 β)-dione-(11,20)]**

ISOLATION:



STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

Diac. 222-4°; $\{[\alpha]_{D}^{25} = +93.6^\circ \pm 3^\circ$ (dioxane) : (1)
 $\{[\alpha]_{D461}^{25} = +113.8^\circ \pm 3^\circ$ (dioxane) : (1)

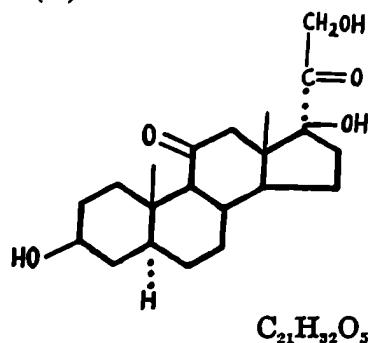
REFERENCES:

1. 83506

17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3(β),17()-DIOL-11-ONE

(Kendall's cpd. "G"; Reichstein's cpd. "D"; Wintersteiner's
cpd. "B"; allo-pregnane-3(β),17(β),21-triol-11,20-dione)

ISOLATION: Ad.: (1,2,3,4,5)



STRUCTURE AND SYNTHESIS: (3,5)

M.P.: 212-4° (u): (4)

230-8°: (2)

228-36° (u): (3)

241-5°: (6) $[\alpha]_D^{16} = +61.8^\circ \pm 2^\circ$; $[\alpha]_{5461}^{16} = +78.7^\circ \pm 2^\circ$ (dioxane): (5)

238-42°: (5)

$[\alpha]_D^{20} = +66^\circ \pm 1.5^\circ$ (alc.): (2)

$[\alpha]_D^{25} = +70.5^\circ$ (alc.): (6)

$[\alpha]_{5461}^{25} = +83^\circ \pm 2^\circ$ (alc.): (3)

PHARMACOLOGY: Corticoid: **52**: Dose? inact.-R (2); **61**: 40γ/kg./day inact.-D (4); **79**: 0.5 mg./day inact.-R (6).

REMARKS: Ppt. with digitonin (5).

DERIVATIVES:

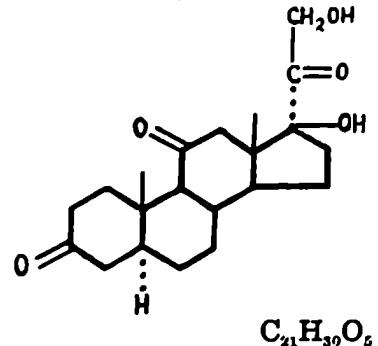
Diac. 224-6°; $\left\{ \begin{array}{l} [\alpha]_D^{16} = +72.3^\circ \text{ (dioxane)} : (5) \\ [\alpha]_{5461}^{16} = +84.7^\circ \text{ (dioxane)} : (5,7) \end{array} \right.$

Semicarb. (+ H₂O) 327-9°: (2)

REFERENCES:

1. 68081
2. 34911
3. 72169
4. 53072
5. 83508
6. A30091
7. A9076
8. A33510

**17(α)-[1-KETO-2-HYDROXYETHYL]-ANDROSTANE-3,11-DIONE-17(β)-OL
(allo-pregnane-3,11,20-trione-17(α),21-diol)**



ISOLATION:

STRUCTURE AND SYNTHESIS:

M.P.:

PHARMACOLOGY: Corticoid: **47A**: up to 25 mg. inact.-R (1)

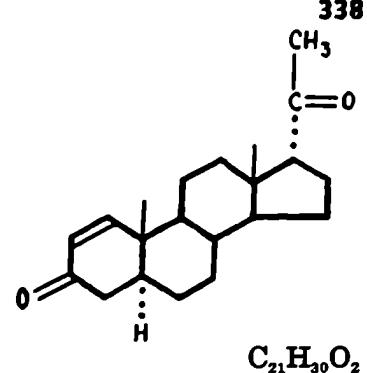
REMARKS: Described in connection with physiological work, without giving chemical characteristics.

DERIVATIVES:

REFERENCES:

1. A31765

**17(α)-[1-KETOETHYL]- Δ^1 -ANDROSTENE-3-ONE
(Δ^1 allo-pregnene-3,20-dione)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 208-9°: (1)
202-4°: (2)

$[\alpha]_D^{21} = + 126^\circ$ (CHCl_3): (2)

PHARMACOLOGY: Luteoid: **49**: 12 mg. ca. as act. as 0.75 mg. of progesterone -Rb (2).

REMARKS: Cpd. previously assigned this structure [m.p. 140° $[\alpha]_D^{23} = + 68.6^\circ$ (alc.)] which in test **48** is inact. up to 1 mg.-Rb (3) is now designated "hetero- Δ^1 -allo-pregnenedione" (2).

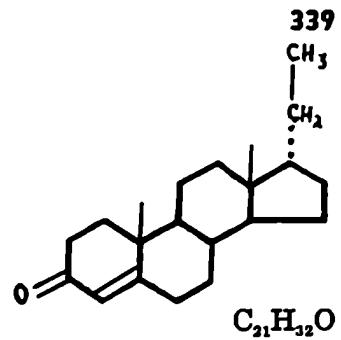
DERIVATIVES:

Dioxime 248-50°: (1)

REFERENCES:

1. 75895
2. A57429
3. 53437

**17(α)-ETHYL- Δ^4 -ANDROSTENE-3-ONE
(Δ^4 -pregnene-3-one)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 90°: (1)

PHARMACOLOGY:

REMARKS:

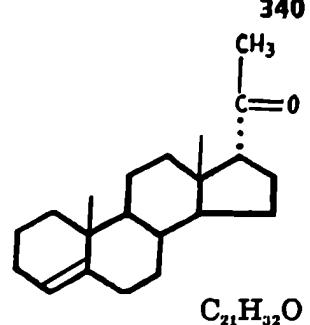
DERIVATIVES:

2:4-dinitrophenylhydrazone 198°: (1)
Semicarb. 216°:(1)

REFERENCES:

1. 75179

**17(α)-[1-KETOETHYL]- Δ^4 -ANDROSTENE
(Δ^4 -pregnene-20-one)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 105° (u): (1)

$[\alpha]_D^{20} = +96.4^\circ$: (1)

PHARMACOLOGY: Luteoid: 49: 0.75 mg. inact.-Rb. (1)

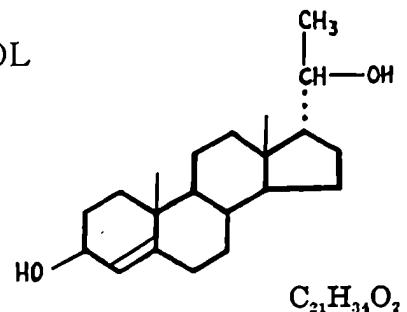
REMARKS:

DERIVATIVES:

REFERENCES:

1. 32392

**17(α)-[1(β)-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3(β)-OL
 $(\Delta^4\text{-}3,20\text{-dihydroxy pregnene})$**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

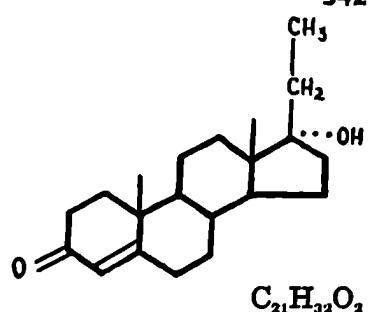
DERIVATIVES:

3-ac,-17 β -bz. 190°; (1)
 17 β -bz. 182°; (1)

REFERENCES:

1. A54801

17(β)-ETHYL-Δ⁴-ANDROSTENE-3-ONE-17(α)-OL
(Ethyl-testosterone, Δ⁴-pregnene-3-one-17(α)-ol)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 143°: (1,2)
 139° (u) : (3)

[α]_D = + 71° (alc.) : (1)

PHARMACOLOGY: Testoid: 29: I.U. = 70-100γ-C (6); 32A: U. > 150γ-C (4,5); 45: s.ves. 145%/
 200γ, 650% / 500γ-R (7).

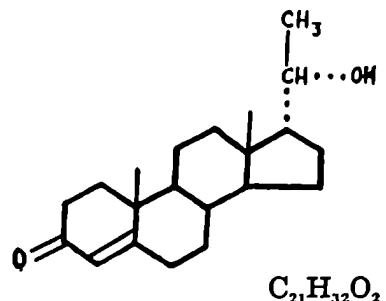
REMARKS: This formula was at first (4) erroneously assigned to the corresponding Δ⁵ cpd.

DERIVATIVES:

REFERENCES:

1. 72151
2. 56783
3. 71848
4. 60176
5. 60175
6. A18098
7. A33511

**17(α)-[1(α)-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE
(dihydro-progesterone; Δ^4 -pregnene-3-one-20(α)-ol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 159° (u) : (1)
158-60°: (2)

$[\alpha]_D^{20} = +89.7^\circ$ (alc.) : (1)

PHARMACOLOGY: Luteoid: **49**: free cpd. and ac. inact. up to 1 mg.-Rb. (1).

REMARKS:

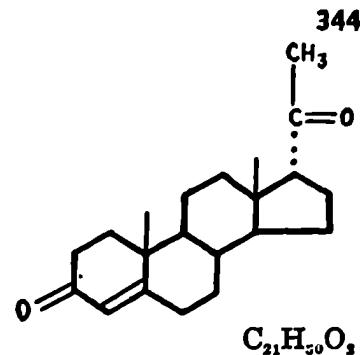
DERIVATIVES:

Ac. 138.5° (u) : (1,2)
Bz.: (3)

REFERENCES:

1. 32390
2. 80967
3. A54804

17(α)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3-ONE
 [Progesterone; Δ^4 -pregnene-3,20-dione; α -form = Wintersteiner &
 Allen's cpd. "B" = Luteosterone C (m.p. 128°); β -form = Winter-
 steiner and Allen's cpd. "C" = Luteosterone D (m.p. 120°)]



ISOLATION: Ov.: (4,9,10,13,16,20,21,23,28,29,81)
 Ad.: (61,79)

STRUCTURE AND SYNTHESIS: (1,2,3,4,5,7,12,15,19,22,24,25,26,27,30,31,32,33,64,81)

BACTERIAL SYNTHESIS: (82).

M.P.: 121-2° (u):	(1,15)	$[\alpha]_{D}^{10} = +174.6^\circ \pm 2^\circ$ (acetone): (52)
120° and 129°:	(10,12,13,14)	$[\alpha]_{D,61}^{10} = +214.7^\circ \pm 2^\circ$ (acetone): (52)
128.5° (u):	(23,25,52)	$[\alpha]_D^{20} = +193.5^\circ$ (alc.): (25,79)
127°:	(2)	$[\alpha]_D^{20} = +200^\circ$ (CHCl_3): (27)
121° and 128.5°:	(6,8,9,27,29)	

PHARMACOLOGY:

Luteoid: I. U. = 1 mg. (68,80); **49,54**: α and β forms equally act. and exhibit no mutual potentiation-Rb. (85); **48**: 0.5-0.75 mg. of both polymorphic forms "definitely" act.-Rb. (8); **49**: U. = 0.75 mg.-Rb. (12); **49**: U. = 1.2 mg., 5 mg., 6 mg., and 0.6-0.7 mg. of enolic ac., pr., n-butyrate and of the free cpd. respectively-act. not prolonged by esterification-Rb. (17,34); **27**: 0.05 I. U. act.-G (54); **46**: U. = 0.25 mg.-Rb. (18); **124**: 5 mg./day act.-Rb. (67); **124**: 1 mg. act.-M (86); **116**: highly act. in inhibiting uterine contractions-Rb. (87); **27**: 1.0 mg. per os act.-G (89); **48**: 50 U. per os definitely act.-Rb. (90); **54**: U. = 1.25 mg.-Rb. (85); **50**: U. = 0.5-5.0 γ -Rb. (73); **136**: act.-G (91,92); **134A**: 0.5-0.75 mg. act.-R (94); **74A**: ca. 10-35 mg. administered parenterally in one or several injections during second half of natural or folliculoid induced cycle (begins about 10th day)-Human (95,96,97); **74A**: about 5 mg./day during second half of natural or folliculoid induced cycle-Human (98,99,100); **134B,134C**: act.-R,M (101,102,103,104).

Testoid: **123**: 200 γ /day inact.-C (4); **64**: 2 mg./day, s.ves. 14%, pta. 326%-R (70); **131**: 1 mg./day, s.ves. 286%, pta. 290%-G (37); **128B**: prep.gl. 105(± 46)%/1 mg., 100(± 15)%/2 mg., 122(± 41)-%/10 mg.-R (111); **132**: 2 mg. inact. on s.ves. and prep.gl.; pta. 208(± 24)%/2 mg.-R (115); **96**: s.ves. 66(± 16)%/2 mg., pta. 286(± 27)%/2 mg., prep.gl. 75(± 10)%/2 mg.-R (115); **125**: at 2 mg. inact. on s.ves. and prep.gl., pta. 395(± 100)%/2 mg.-R (115); **114**: 10 mg. inact. on s.ves. and prep.gl., pta. 90%/10 mg.-R (75).

Folliculoid: **62**: 2 mg. of enol ac. inact.-M (34); **3**: *Metrotropic* act. 1/500 that of estrone-M (55); **7,10**: 400 γ inact.-R (63); **115**: *Mammotropic* U. = 1 mg.-M (88); **128C**: 10 mg./day vag. mucifying, stratifying or cornifying-R (71); **30**: up to 1 mg. inact.-C (93); **128A**: *Anti-castration cell* act.: 1 mg. inact., +/2 mg., + - + +/10 mg.-R (111,112); **132**: *Anti-castration cell* act.: + + +/10 mg.-R (112); **128A**: *Metrotropic* act.: 92.6(± 32)%/1 mg., 107 (± 9)%/2 mg., 75(± 15)%/10 mg.-R (111); **133B**: *Anti-Leydig cell* act.: +/1 mg., + + +/10 mg.-R (76).

Corticoid: **97**: 1 mg. act.-M (46); **84**: as act. as D.C.A. at 1 mg./day dose level -R (43,49); **53A**: 4 mg. necessary for life maintenance-R (24,53,41); **52**: 2-4 mg./day inact.-R (38,47); **47A**: up to 45 mg. inact.-R (48,57); **47B,47C**: act. only with doses of 10 mg. or more/day-R (57); **84**: 4 mg. act.-R (51); **82**: up to 12 mg. inact.-D (47); **15**: 10 mg./day act. in ♀/c or ♂ but not in ♀, it also restores normal CHO levels in ♂ but not in ♀-Cat (39,40); **72**: 2 mg./day act. in ♂ and ♀ Ferret (44,45); **79**: 1-2 mg./day act in 50% of animals.-R (50); **87**: 5 mg. inact.-R (50); **119**: 2-5 mg./day slightly act. and does not inhibit lactation-R (113); **146**: 2 mg. inact.-M (11).

Anti-Folliculoid: **38**: inhibits vag. cornification caused by folliculoids-M,R (60,86,105); **134D**: act.-R, Rb. (102,106,107,108,110,114,94); **144**: act.-Monkey (109); **129**: Hyp. +20(± 1)%/2 mg., -14(± 6)%/

10 mg.; Ad. +11(±19)%/2 mg., +30(±4)%/10 mg.; Te. +26(±9)%/2 mg., +42(±6)%/10 mg.
-R(72).

Gonadotropic: **21**: 0.25 mg. act.-X(50); **125**: Te. 75(±18)%/2 mg.-R(115).

Renotropic: moderately act. in intact. and hypx.-R(77).

Diuretic: causes diuresis in intact and hypx.-R(84).

Anesthetic: **11**: U. = 2 mg.-R (58); **127**: U. = 0.25 mg.-Fish (78).

REMARKS: Exists in 2 polymorphic forms (β) m.p. 121° and (α) 128.5° (59); "Neo-progesterone" is a member of D-homo series (65,66,69); Enol ac. is $\Delta^{3,5}$ -diene (34); "Photoproduct" obtained by ultraviolet irradiation due to doubling of molecule and masks α,β unsaturated ketone group (83).

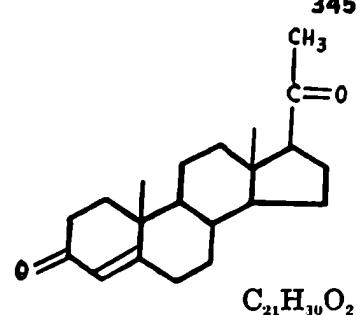
DERIVATIVES:

3-enol ac.	138° (u);	$[\alpha]_D^{20} = -42^\circ$ (CHCl ₃):	(17,34)
Dioxime	244°:		(4,8,12,26,59)
3-enol pr.	134-6° (u);	$[\alpha]_D^{20} = -40.6^\circ$ (CHCl ₃):	(34)
3-enol n-butyrate	116-8° (u);	$[\alpha]_D^{20} = -37.8^\circ$ (CHCl ₃):	(34)
Disemicarb.	280°:		(29)
17-Br. pyridinium cpd.	265-8°:		(35)
17 ² -Cl.	203-5°;	$\begin{cases} [\alpha]_D^{24} = +209.5^\circ \pm 6^\circ & (\text{CHCl}_3) \\ [\alpha]_{5461}^{24} = +255.2^\circ \pm 7^\circ & (\text{CHCl}_3) \end{cases}$:	(30,35,36)
17 ² -Br.	190-1°:		(35)
17 ² -I	.		(30)
17 ² -diazo	182-4°:		(36)
Sulphonic acid ester	190-2°:		(62)
17 ² -benzal	155-8°:		(74)
17 ² -benzyl	86-8°:		(74)
17 ² -Cl.-pyridinium cpd.	274-5°:		(35)
Sulphonic acid me. ester	160-1°:		(62)
"Photoproduct"	340°;	$[\alpha]_D^{23} = +107^\circ$ (CHCl ₃):	(83)
Oxime of "Photoproduct"	390-400°:		(83)

REFERENCES:

- | | | | | |
|------------|------------|------------|------------|-------------|
| 1. A15309 | 24. A34070 | 47. 75612 | 70. A34176 | 93. 73572 |
| 2. 77142 | 25. 32392 | 48. A31765 | 71. A37486 | 94. 76422 |
| 3. 77857 | 26. 30203 | 49. A34177 | 72. A37637 | 95. A36125 |
| 4. 27944 | 27. 32301 | 50. 76301 | 73. 75634 | 96. 76824 |
| 5. A34410 | 28. 30126 | 51. 75213 | 74. 83175 | 97. 83220 |
| 6. 27943 | 29. 30175 | 52. 83506 | 75. A38071 | 98. A37073 |
| 7. 75054 | 30. 78850 | 53. 75963 | 76. A38086 | 99. A57992 |
| 8. 30224 | 31. 79003 | 54. A7923 | 77. A35219 | 100. 14731 |
| 9. 30127 | 32. 80962 | 55. A35939 | 78. A38070 | 101. A58195 |
| 10. 20044 | 33. 80967 | 56. 75731 | 79. A19193 | 102. A36512 |
| 11. A30403 | 34. 71658 | 57. A37373 | 80. A56335 | 103. A35972 |
| 12. 20442 | 35. 76734 | 58. A36744 | 81. A54801 | 104. A31649 |
| 13. 20307 | 36. 78856 | 59. 32393 | 82. A57195 | 105. A2568 |
| 14. 27945 | 37. A38456 | 60. 72400 | 83. A57497 | 106. 77168 |
| 15. 35301 | 38. A9077 | 61. 73594 | 84. A32813 | 107. 76422 |
| 16. A7802 | 39. 77429 | 62. A57430 | 85. 56308 | 108. 27876 |
| 17. 66860 | 40. A30208 | 63. 55958 | 86. A36553 | 109. 69629 |
| 18. A50335 | 41. A31045 | 64. 75060 | 87. 38584 | 110. 38584 |
| 19. A17900 | 42. A30408 | 65. 79620 | 88. A36499 | 111. A56752 |
| 20. 31105 | 43. A30167 | 66. 75678 | 89. A34940 | 112. A37513 |
| 21. 45341 | 44. A19255 | 67. A38372 | 90. A50831 | 113. A38216 |
| 22. 60174 | 45. A18250 | 68. A36596 | 91. A30263 | 114. 31107 |
| 23. 60177 | 46. A35567 | 69. 75743 | 92. A54671 | 115. 100000 |

**17(β)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3-ONE
(iso-progesterone; Δ^4 -pregnene-3,20-dione)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 145°: (1)

$[\alpha]_D = 0^\circ$ (alc.): (1)

PHARMACOLOGY: Luteoid: 49: inact. up to 0.9 mg.-Rb.(1).

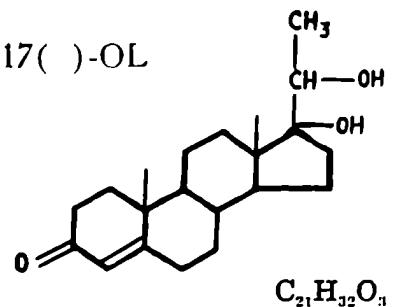
REMARKS:

DERIVATIVES:

REFERENCES:

- 1. A54237

**17()-[1()-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE-17()-OL
 (Δ^4 -pregnene-17,20-diol-3-one)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 199° (u): (1)
 204-5°: (2)

PHARMACOLOGY:

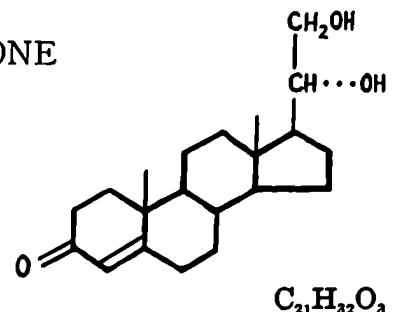
REMARKS:

DERIVATIVES:

REFERENCES:

1. 71848
2. 84060

**17(β)-[1(α),2-DIHYDROXYETHYL]-Δ⁴-ANDROSTENE-3-ONE
 (Δ⁴-pregnen-3-one-20(α),21-diol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 166-7°: (1)

$[\alpha]_D^{20} = +92.6^\circ \pm 1^\circ$ (alc.): (1)

PHARMACOLOGY: Corticoid: **52:** 2 mg./day inact.-R⁽¹⁾.

REMARKS:

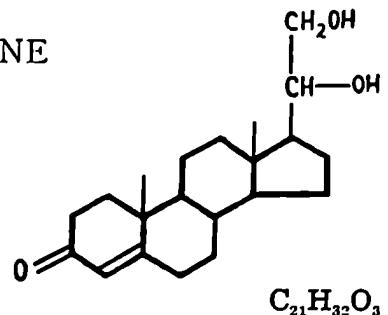
DERIVATIVES:

Monoacetone cpd. 126°; $[\alpha]_D^{20} = +91.5^\circ \pm 1^\circ$ (acetone): (1)

REFERENCES:

1. 72133

**17(β)-[1(β).2-DIHYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE
 (Δ^4 -pregnen-3-one-20(β),21-diol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 183-5°: (1)

PHARMACOLOGY:

REMARKS:

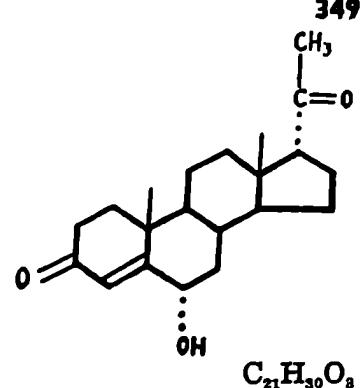
DERIVATIVES:

Monocetone cpd. 132°; $[\alpha]_{\text{D}}^{20} = +70.5^\circ$: (1)

REFERENCES:

1. 72133

**17(α)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3-ONE-6(α)-OL.
(6(α)-hydroxy progesterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,5)

M.P.:

PHARMACOLOGY:

Corticoid: **47A**: Preliminary tests suggested possible act. of ac. at 2 mg./day-R (2); **47A**: ac. up to 2 mg./day inact.-R (3).

Luteoid: **54**: 3 mg. of ac. act.-Rb. (2); **46**: 5 mg. of ac. of doubtful act.-Rb. (7).

Folliculoid: **55**: Ac. probably vag. cornifying -R (4).

Anesthetic: **11**: U. < 5 mg. of ac.-R (4,6).

REMARKS:

DERIVATIVES:

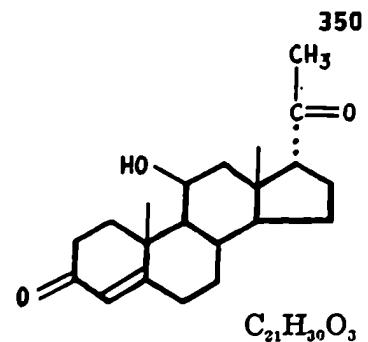
6-ac. 145-6°; $[\alpha]_D^{17.5} = +89.7^\circ$ (alc.): (1,2)

Ac. (amorphous); $\begin{cases} [\alpha]_D^{22.5} = +106.7^\circ \text{ (alc.)} : & (5) \\ [\alpha]_D^{22.5} = +104^\circ \text{ (acetone)} : & (5) \end{cases}$

REFERENCES:

1. 77239
2. 78699
3. A37373
4. A36744
5. S1867
6. A38070
7. A56335

**17(α)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3-ONE-11(β)-OL
(11-hydroxy-progesterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 187-8°: (1,2)

[α]_D¹⁷ = + 222.5° ± 4° (acetone): (1)

PHARMACOLOGY: Luteoid: **48**: 3 mg. inact.-Rb. (1); **50**: 200 γ inact.-Rb. (1).

REMARKS:

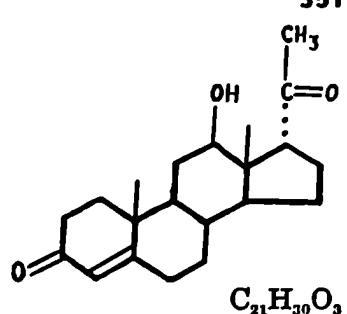
DERIVATIVES:

17²-Cl (impure): (1)
17²-I (impure): (1)

REFERENCES:

1. 78850
2. 81151

**17(α)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3-ONE-12(β)-OL
(12-hydroxy-progesterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.: 164-7° + 195-8°: (2)
195° : (3)
198-200° : (4)

$[\alpha]_D^{15} = + 205^\circ \pm 4^\circ$ (acetone) : (2)
 $[\alpha]_{5461}^{15} = + 239^\circ \pm 4^\circ$ (acetone) : (2)

PHARMACOLOGY: Luteoid: Test? "trace of act." - Species ?(1)

REMARKS:

DERIVATIVES:

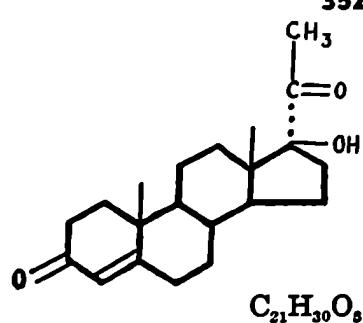
Ac.: (1)

Bz.: 164-6°; $[\alpha]_D^{15} = + 96.2^\circ \pm 2^\circ$ (acetone) : (1)

REFERENCES:

1. A34408
2. S1151
3. A36511
4. 84186

**17(α)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3-ONE-17(β)-OL
(17(β)-hydroxy-progesterone)**



ISOLATION: Ad.: (2,3,4)

STRUCTURE AND SYNTHESIS: (1,2,3,5).

M.P.: 222-3° + 276°: (4)

218-20°: (5)

212-5°: (2,3)

$[\alpha]_D^{27} = +102^\circ \pm 3^\circ$ ($CHCl_3$): (2,3)

$[\alpha]_D^{17} = +105.6^\circ \pm 2^\circ$ ($CHCl_3$): (4)

$[\alpha]_D^{17} = +98.8 \pm 5^\circ$ (acetone): (5)

PHARMACOLOGY:

Corticoid: **47A:** Up to 3 mg. (twice daily) inact.-R (3,6); **Test?:** dose? questionably act. (2); **53A:** 0.25 mg./day inact.-R (3).

Testoid: **106:** s.ves. 57%/166 γ ; pta. 155%/166 γ -R (2,3); **41:** 200 γ /day inact.-C (3).

Luteoid: **48:** 5 mg. inact.-Rb. (2,3).

REMARKS:

DERIVATIVES:

Disemicarb. (ca.) 360° : (2)

Dioxime 250-1°: (2)

REFERENCES:

1. 77310

2. A33916

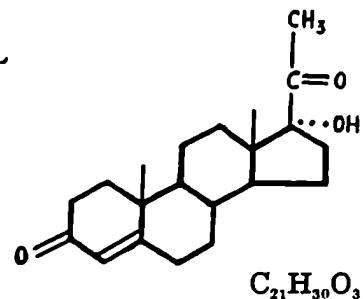
3. A37407

4. 81793

5. 81065

6. A37373

**17(β)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3-ONE-17(α)-OL
(17(α)-hydroxy-progesterone)**



ISOLATION:

M.P.:

PHARMACOLOGY: Luteoid: **86A:** 30 mg. of ac. act.-Rb. (5).

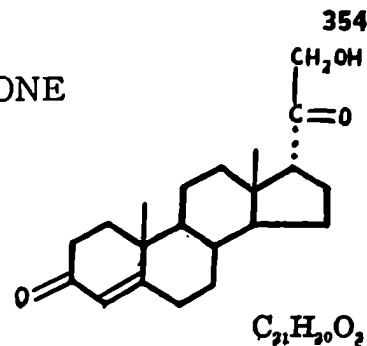
REMARKS: Cpd. of m.p.284-8° had been assigned this structure (1), but later the cpd. in question was shown to be 17a()-methyl- Δ^4 -D-homoandrostene-3,17-dione-17a-ol (2).

DERIVATIVES:

17¹-Anil 221-3°; $[\alpha]_D = -19^\circ \pm 1^\circ$ (CHCl₃): (3).
Ac. 198-200; $[\alpha]_D = +66^\circ$ (dioxane): (1,4) 2. 75679
3. 77143
4. 84189
5. 75678

REFERENCES:

1. 73580
2. 75679
3. 77143
4. 84189
5. 75678



17(α)-[1-KETO-2-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE
 (desoxycorticosterone, Reichstein's cpd."Q", Kendall's
 desoxy cpd."B", 21-hydroxy-progesterone)

ISOLATION: Ad.: (3)

STRUCTURE AND SYNTHESIS: (2,4,5,7,37,45,56)

M.P.: 140-2°: (3)
 141-2°: (5,10)

$[\alpha]_D^{22} = +178^\circ \pm 3^\circ$ (alc.): (5)

PHARMACOLOGY:

Corticoid: **52:** 80 γ of ac./day s.c. or 240 γ /day percutaneously act., while 500 γ per os inact. -R (41,43); **52:** 800 γ of ac./day act.-R (5); **112:** 0.5 mg. of ac. act.-R (41); **88:** 10 mg. of free cpd. act., esterification especially with palmitic or benzoic acid prolongs act.-R (9); **82:** $\frac{1}{16}$ - $\frac{1}{4}$ mg./7-12 kg. of ac. act.-D (41); **61:** free cpd. and its ac. are respectively 6-10 and 15-20 times more act. than corticosterone-D (14); but in **47B:** they are less act. than the latter-R (15); **47C:** 60 γ of free cpd. act. while ac. inact at the same dose-R (27,31); **47A:** At 1-5 mg. free cpd. and ac. slightly act., free cpd. > ac.-R (17,42); **53A:** 0.25-1 mg. of ac. act.-R (33,35); **95:** 1-1.5 mg. of ac./day/10 kg. act.-D (26); **15:** ca. 3 mg./kg. of ac. later decreased to 1 mg./kg. act.-Cat (24); **94:** 0.5-1 mg. of ac./day act.-G (25); **108:** act. of ac. < water soluble corticoids-R (16); **47C, 52:** Na phosphate as act. as free cpd.-R (29,30); **52:** ac. and phosphate inact. *per os* whether given in oil or alc., although phosphate act. s.c.-R (40); **53A:** 0.3-0.4 mg. of ac./day act.-R (12); **Test?** water soluble glucoside as act. as free cpd.-R (59); **87:** 4 mg. act.-R (60). "5-10 mg. of ac. daily parenterally in oil beneficial in Addison's disease"-Human (70,71,72); **119:** 0.1-2 mg./day of ac. helpful in some animals but "in no case maintained lactation equal to the average control figure"-R (73); **148:** 2 mg. of free cpd. and ac. slight act. if any-M (76).

Luteoid: **124:** 20 γ of ac./day act.-Rb. (44); **124:** 3 mg./day of ac. act.-M (68); **48:** U. = 1-1.2 mg. of ac.-Rb. (13); **49:** U. = 6 mg. of ac.-Rb. (22); **86B:** 10 mg./day of ac. act.-Rb. (13,67); **86B:** 80 mg. of ac. inact.-Rb. (22); **27:** 1/10 of ac. as act. as progesterone-G (38); **46:** U. = 3-6 mg. of ac.-Rb. (38); **89:** 1 mg./day of ac. act.-Cat (34,18); **91:** U. = 5 mg. of ac.-Rb. (20); **48:** U. = ca. 7.5 mg. of ac.-Rb. (43); **100A:** 5 mg./day of ac. act.-Opossum (36); **100B:** 5 mg./day of ac. inact.-Opossum (36); **46:** U. = 2.5 mg. of ac.-Rb. (57); **48:** U. < 10 mg. of ac.-Rb. (9); **46:** U. = 0.25-0.5 mg. of ac.-Rb. (58); **116:** 5-10 mg. of ac. inhibits uterine contractions-Rb. (68); **74A:** 300 mg. of ac. act.-♀ Human (61); **136:** 10 mg. act.-G (69).

Folliculoid: **90:** 0.5-2 mg. of ac. act.-R (19); **101:** 10 mg. of ac./day act.-Monkey (32); **55:** Ac. possesses slight vag. cornifying act.-R (39,40); **74B:** 5-10 mg. of ac. 2 \times a week act. ♀-Human (66); **128A:** 10 mg. of ac./day very slightly act.-R (28); **128C:** Ac. possesses slight vag. cornifying act.-R (52); **60:** 0.5 γ of ac. act., ac. more act. than free cpd.-B (50); **133B:** Anti-Leydig cell act.: +/1 or 10 mg./day-R (47); **128A:** metrotropic act. 44(± 11)/2 mg., 81(± 20)%/10 mg.; anti-castration cell act. up to 10 mg.inact.-R (28); **132:** Anti-castration cell act. + +/10 mg.-R (74).

Testoid: **92:** 1.4 mg. of ac. act.-C (20); **93:** 1 mg./day of ac. inact.-G (21); **34:** 1-2 mg./day of ac. inact.-R (21); **57:** act. of ac. slight if any-R (40); **131:** 3 mg./day of ac. inact.-G (61); **128B:** prep.

gl. 24(± 6)%/2 mg., 43(± 15)%/10 mg.-R (28); **132**: 2 mg. inact. on s.ves., pta., and prep.gl.-R (55); **96**: inact. on s.ves. and pta.; prep.gl. 67(± 12)%/2 mg.-R (75); **125**: inact. on s.ves. and pta., prep.gl. 54(± 9)%/2 mg.-R (75).

Anti-folliculoid: **103**: 0.5-2 mg./day of ac. inhibits vag. cornification caused by "0.5 U. of estradiol /day-R (23); **120**: 0.75 mg. of ac. inhibits vag. act. of 0.05 of estradiol-M (68); **129**: 10 mg. inact.-R (53).

Gonadotropic: **125**: 2 mg./day inact.-R (75).

Renotropic: Ac. moderately act. in intact and hypx.-R (63); ac. causes nephrosclerosis in Chick, Monkey, D, and R (64,65); **145**: 16%/7.3 mg.-M (75).

Diuretic: **98**: ac. act.-R (1,62).

Anesthetic: **11**: U. = 1 mg. of ac.-R (40); **127**: U. = 0.5 mg. of ac.-Fish (48).

REMARKS:

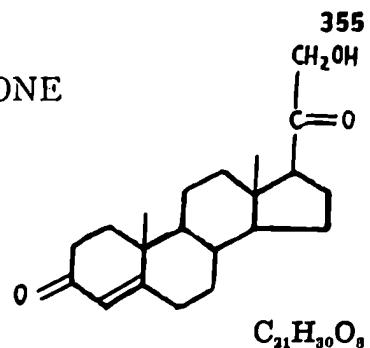
DERIVATIVES:

Ac.	$\left\{ \begin{array}{l} 161-2.5^\circ; \\ \end{array} \right.$	$[\alpha]_D^{10} = +173.6^\circ$; $[\alpha]_{5461}^{10} = +212^\circ$ (dioxane): (54). $[\alpha]_D^{18} = +164^\circ$; $[\alpha]_{5461}^{18} = +200^\circ$ (acetone): (54). $[\alpha]_D^{10} = +177^\circ \pm 4^\circ$ (alc.): (2,3,5,6,8,9,37) $[\alpha]_D^{10} = +182^\circ \pm 4^\circ$ (alc.); $[\alpha]_{5461}^{10} = +221^\circ \pm 3^\circ$ (alc.): (56).
Pr.		163-4°: (9)
n-butyrate		110-1°: (9)
n-valerate		84-5°: (9)
Palmitate		60-1°: (1)
Bz.		209-10°: (9)
17 ² -tosylate		170-1°: (11,30)
17 ² -Na. phosphate		: (30)
Tetra-acetyl- β -glucoside		: (46)
Glucoside		: (49)

REFERENCES:

- | | | | | |
|------------|------------|------------|------------|------------|
| 1. A31897 | 16. A32766 | 31. A33452 | 46. A54238 | 61. A38456 |
| 2. 76735 | 17. 77519 | 32. A35195 | 47. A38086 | 62. A33566 |
| 3. A19374 | 18. 78103 | 33. A34971 | 48. A38070 | 63. A35219 |
| 4. A8218 | 19. 79053 | 34. A33855 | 49. A38749 | 64. A56583 |
| 5. A9077 | 20. 79054 | 35. A34177 | 50. A38963 | 65. A55847 |
| 6. 78851 | 21. 79056 | 36. 80860 | 51. A39520 | 66. A30227 |
| 7. A35088 | 22. A32096 | 37. 81148 | 52. A37480 | 67. A54926 |
| 8. 76734 | 23. A34002 | 38. A30234 | 53. A37637 | 68. 78159 |
| 9. 72685 | 24. A36198 | 39. 78069 | 54. 83506 | 59. A54671 |
| 10. A19372 | 25. A35786 | 40. A36744 | 55. A38071 | 70. A33500 |
| 11. 78850 | 26. 75075 | 41. 75612 | 56. 79195 | 71. A35224 |
| 12. 79195 | 27. A33857 | 42. A31765 | 57. A50335 | 72. A34216 |
| 13. A18138 | 28. A56752 | 43. 75671 | 58. 74769 | 73. A38216 |
| 14. 74850 | 29. 80444 | 44. A38372 | 59. A56996 | 74. A37513 |
| 15. 77274 | 30. 78853 | 45. A54237 | 60. A37457 | 75. 100000 |
| | | | | 76. A36403 |

**17(β)-[1-KETO-2-HYDROXYETHYL]-Δ⁴-ANDROSTENE-3-ONE
(17-Iso-desoxycorticosterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 179-81°: (1)

$[\alpha]_D^{10} = -6^\circ \pm 2^\circ$ (alc.) : (1)

$[\alpha]_{5461}^{10} = -9^\circ \pm 2^\circ$ (alc.) : (1)

PHARMACOLOGY: Corticoid: **53A:** 1 mg. of ac./day inact., while under similar conditions 0.3-0.4 mg. D.C.A. act.-R (1).

REMARKS:

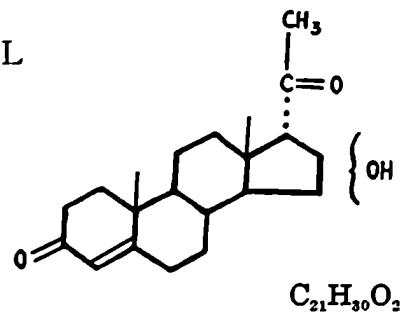
DERIVATIVES:

Ac. 137° + 174°; $\begin{cases} [\alpha]_D^{17} = -26^\circ \text{ (acetone)} : & (1) \\ [\alpha]_{5461}^{17} = -32^\circ \pm 2^\circ \text{ (acetone)} : & (1) \end{cases}$

REFERENCES:

1. 79195

**17(α)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3-ONE-? (β) -OL
 $(\Delta^4$ -pregnene-? (β) -ol-3,20-dione)**



ISOLATION:

M.P.: I. 185° : (1)
 II. 184° : (1)

I. $[\alpha]_{D}^{20} = +186^\circ \pm 10^\circ$ (alc. $^\circ$: (1))
 II. $[\alpha]_{D}^{20} = +40^\circ \pm 10^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS: Two isomers (1)

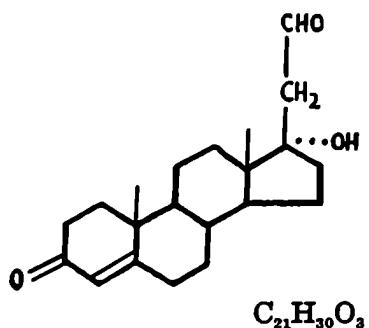
DERIVATIVES:

Ac. of I. 198° : (1)

REFERENCES:

I. A57401

**17(β)-[2-ALDOETHYL]-Δ⁴-ANDROSTENE-3-ONE-17(α)-OL
(Testosterone-17-acetaldehyde; Δ⁴pregnene-3-one-17(α)-ol-21-al)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 149-51°: (1)
142-3°: (2)

$[\alpha]_D^{18} = +83^\circ$ (alc.): (1)

PHARMACOLOGY:

REMARKS:

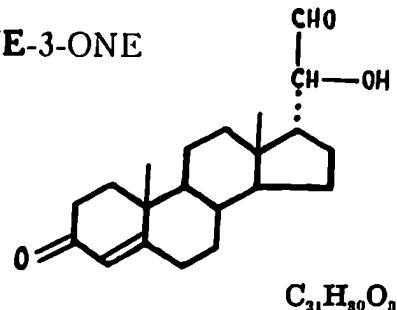
DERIVATIVES:

Dioxime 215°: (1)
Dioxime (-·H₂O) 141° + 208-10°: (2)

REFERENCES:

1. 75741
2. 75052

**17(α)-[1(β)-HYDROXY-2-ALDOETHYL]- Δ^4 ANDROSTENE-3-ONE
(Δ^4 -pregnene-3-one-20(β)-ol-21-al).**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 206-8°: (1)

$[\alpha]_D^{20} = +84^\circ \pm 2^\circ$ (dioxane): (1)

PHARMACOLOGY:

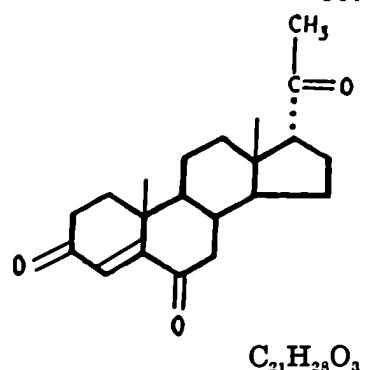
REMARKS:

DERIVATIVES:

Disemicarb.	> 300°:	(1) 1. 81148
17 ¹ -ac.	255-6°; $[\alpha]_D^{20} = +56^\circ \pm 2^\circ$ (dioxane): (1)	
Dime-acetal	135-6°; $[\alpha]_D^{18} = +62.1^\circ \pm 2^\circ$ (acetone): (1)	
Ac.-dime.-acetal	112-3°; $[\alpha]_D^{15} = +111^\circ \pm 4^\circ$ (methanol): (1)	
Dime.-acetal-semicarb.	220-2°:	(1)

REFERENCES:

**17(α)-[1-KETOETHYL]- Δ^1 -ANDROSTENE-3,6-DIONE
(6-keto-progesterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 185-8°: (1)

PHARMACOLOGY: **Luteoid:** 54: 5 mg. inact.-Rb. (1).

Folliculoid: 62: 1 mg./day act.-M (1).

REMARKS:

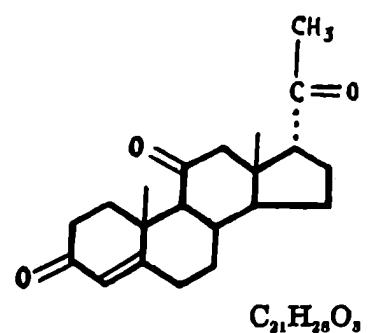
DERIVATIVES:

17²-Cl 215-20°: (2)

REFERENCES:

1. 78698
2. A9077

**17(α)-[1-KETOETHYL]- Δ^4 -ANDROSTENE-3,11-DIONE
(11-keto-progesterone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 172-4°: (1)
173-5: (2)

$[\alpha]_D^{17} = +238.5^\circ \pm 8^\circ$ (acetone): (1)
 $[\alpha]_D^{18} = +243.5^\circ \pm 6^\circ$ (acetone): (2)
 $[\alpha]_{5461}^{18} = +283^\circ \pm 6^\circ$ (acetone): (2)

PHARMACOLOGY:

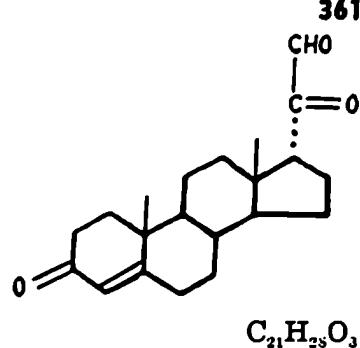
REMARKS:

DERIVATIVES:

REFERENCES:

1. 78850
2. 84185

**17(α)-[1-KETO-2-ALDOETHYL]- Δ^4 -ANDROSTENE-3-ONE
(Δ^4 -3-ketoandrostanyl-glyoxal-17)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 104-6°: (1)

PHARMACOLOGY: Corticoid: **52**: 2.5 mg./day quite act., 1 mg. (crude product) inact.-R (1).

REMARKS:

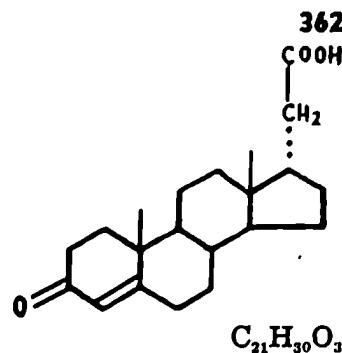
DERIVATIVES:

Dime. acetal 84-6°; $\{[\alpha]_{D}^{21} = +170.3^\circ \pm 2^\circ$ (acetone): (1) 1. 76734
 $[\alpha]_{D461}^{21} = +207^\circ \pm 3^\circ$ (acetone): (1) 2. 81148
 Dict. mercaptal 94-6°; $[\alpha]_{D}^{20} = +258^\circ \pm 6^\circ$ (acetone): (2)

REFERENCES:

**17(α)-CARBOXYMETHYL- Δ^4 -ANDROSTENE-3-ONE
(Δ^4 -pregnene-3-one-21-acid)**

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ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

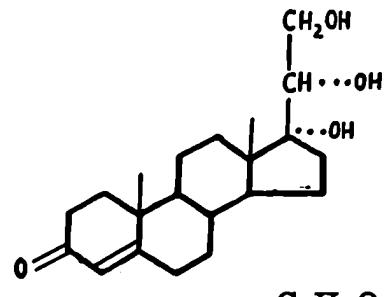
DERIVATIVES:

Me. ester 146-7°; $[\alpha]_D = +84^\circ \pm 1^\circ$ (dioxane); (1)

REFERENCES:

1. 77141

17(β)-[1(α),2-DIHYDROXYETHYL]-Δ⁴-ANDROSTENE-3-ONE-17(α)-OL
(Δ⁴-pregnene-3-one-17(α),20(α),21-triol)



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

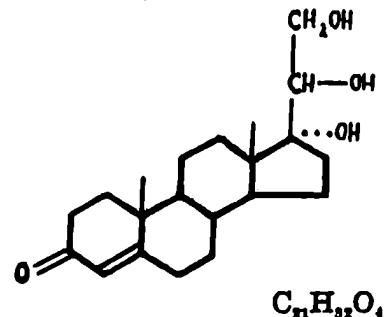
REMARKS:

DERIVATIVES:

17¹,17²-diac. 165-6°; $[\alpha]_{\text{D}}^{15} = +22^\circ \pm 3^\circ$ (acetone); (1) 1. 81696
 17¹,17²-monoacetone cpd. 220-1.5°; $[\alpha]_{\text{D}}^{15} = +67^\circ \pm 2^\circ$ (acetone); (1)

REFERENCES:

**17(β)-[1(β),2-DIHYDROXYETHYL]-Δ⁴-ANDROSTENE-3-ONE-17(α)-OL
(Δ⁴-pregnen-3-one-17(α),20(β),21-triol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2)

M.P.: 233-5°: (1)

$[\alpha]_{\text{D}}^{20} = +65.5^\circ$ (dioxane) : (1)

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

Semicarb. 216-8°:

REFERENCES:

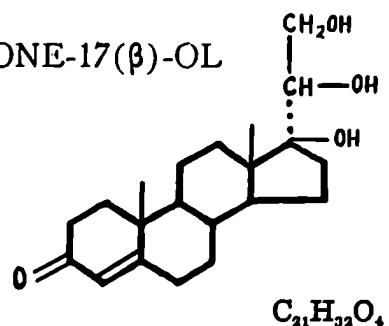
(1) 1. A36445

17¹,17²-diac. { 178-9°; $[\alpha]_{\text{D}}^{20} = +43.6^\circ$ (dioxane) : (1)
180-1°; $[\alpha]_{\text{D}}^{16} = +50.2^\circ \pm 2^\circ$ (acetone) : (2)

(2) 2. 81696

Acetone cpd. 173-5°; $[\alpha]_{\text{D}}^{17} = +39.3^\circ \pm 2^\circ$ (acetone) : (2)

**17(α)-[1(β),2-DIHYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE-17(β)-OL
(17(β)-pregnenetriolone)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,3,6)

M.P.: 189-90°: (1,6)

$[\alpha]_D = +63^\circ$ (dioxane): (1,2)

PHARMACOLOGY: Corticoid: **15**: 15 mg. inact.-Cat (1); **47B,47C**: up to 5 mg./day inact.-R (2).
Luteoid: **48**: 15 mg. inact.-Rb. (1).

REMARKS:

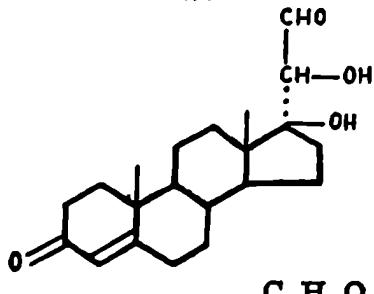
DERIVATIVES:

17¹,17²-diac. { 171° and 194° (polymorphic): (5)
189-90°; $[\alpha]_D^{20} = +125^\circ$ (dioxane): (1)

REFERENCES:

1. A35089
2. A33452
3. A36445
4. 81696
5. 79195
6. 75080

**17(α)-[1(β)-HYDROXY-2-ALDOETHYL]- Δ^4 -ANDROSTENE-3-ONE-17(β)-OL
(Δ^4 -pregnene-3-one-17(β),20-diol-21-al)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1,2,3)

M.P.:

PHARMACOLOGY:

REMARKS:

DERIVATIVES:

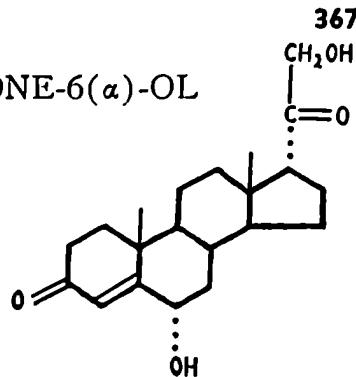
17¹-ac. 206-8°; $[\alpha]_D^{18} = +119^\circ \pm 3^\circ$ (dioxane): (1)
Semicarb.-ac. mixture 190°: (1)

REFERENCES:

1. 79193
2. 79192
3. A54803

**17(α)-[1-KETO-2-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE-6(α)-OL
(6(α) hydroxy-11-desoxycorticosterone)**

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ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

Corticoid: **109**: up to 2 mg./day of diac. inact.-R (1); **47A**: up to 2 mg. of diac. inact.-R (1,2); **47C**: 0.5 mg./day of diac. act.-R (1,2).

REMARKS: Diac. may undergo molecular rearrangement to cpd. of M.P. 120-1°, which is an anesthetic in test II; U.: > 3 mg.-R (3).

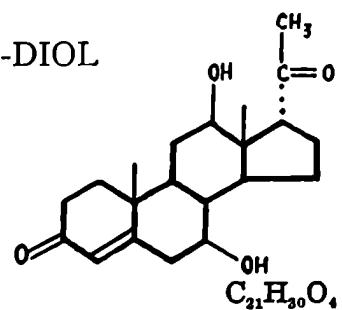
DERIVATIVES:

Diac. 84-8°; $[\alpha]_D^{27} = +114^\circ$ (acetone): (1)

REFERENCES:

1. A36074
2. A37373
3. A38070

**17(α)-[1-KETOETHYL]-Δ⁴-ANDROSTENE-3-ONE-7(),12()-DIOL
 (Δ⁴-pregnene-3,20-dione-7(),12()-diol)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

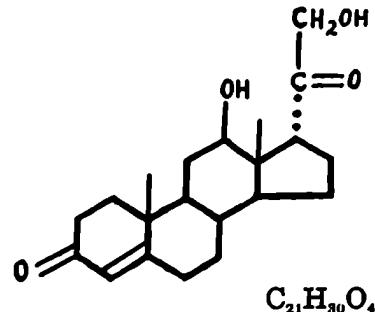
DERIVATIVES

Diac. 249-52°: (1)

REFERENCES:

1. A54241

**17(α)-[1-KETO-2-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE-12(β)-OL
[Pregnene-(4)-diol-(12 β ,21)-dione-(3,20)]**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 90-124° (+H₂O?) : (1)

$[\alpha]_D^{21} = +186.1^\circ \pm 2^\circ$ (dioxane) : (1)

$[\alpha]_{5461}^{21} = +221.1^\circ \pm 2^\circ$ (dioxane) : (1)

PHARMACOLOGY:

Corticoid: 52: 0.5 mg./day of 17²-ac. and 3 mg./day of diac. inact.-R (1); 146: up to 4 mg. of diac. inact.-M (1).

REMARKS:

DERIVATIVES:

17 ² -ac.	182-4°; $\{ [\alpha]_D^{21} = +203.7^\circ \pm 2^\circ$ (acetone) : (1)
	$[\alpha]_{5461}^{21} = +251.6^\circ \pm 2^\circ$ (acetone) : (1)
Diac.	158-9°; $[\alpha]_D^{17} = +197.7^\circ \pm 5^\circ$ (acetone) : (1)
12-ac.	188-92°; $\{ [\alpha]_D^{10} = +185.3^\circ \pm 2^\circ$ (acetone) : (1)
	$[\alpha]_{5461}^{10} = +226.3^\circ \pm 3^\circ$ (acetone) : (1)

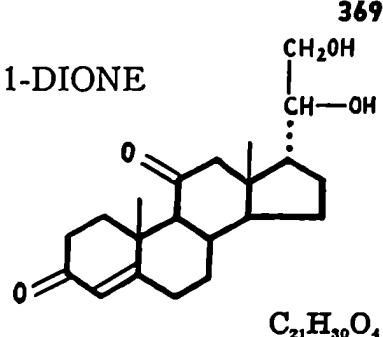
REFERENCES:

1. 84187

**17(α)-[1(β),2-DIHYDROXYETHYL]- Δ^4 -ANDROSTENE-3,11-DIONE
(Reichstein's cpd. "T")**

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ISOLATION: Ad.: (1,2)



PHARMACOLOGY:

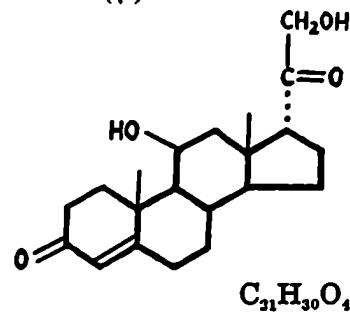
DERIVATIVES:

Diac. 212-3°: (1,2).

REFERENCES:

1. 76731
2. A19374

M.P.:

17(α)-[1-KETO-2-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE-11(β)-OL(Corticosterone, 11,21-dihydroxy-progesterone, Kendall's
cpd. "B", Reichstein's cpd. "H")

ISOLATION: Ad. (1,4,5,6,11,12).

STRUCTURE AND SYNTHESIS: (1,2,5,6,7,8,14).

M.P.: 177-80° (u) : (5,13) $[\alpha]_D^{25} = +222^\circ$ (alc.) ; $[\alpha]_{5461}^{25} = +258^\circ \pm 3^\circ$ (alc.) : (5).
 181-2°: (4,6,10,11) $[\alpha]_D^{15} = +223^\circ$ (alc.) : (4,6,10,11).

PHARMACOLOGY: Corticoid: **82**: 0.6 mg. act.-D (3,17); **112**: 0.5-1 mg. act.-R (3,17); **52**: 1.2 mg. act.-R (17); **82**: 2-3 mg. of ac., 2-3 mg. of butyrate act., while 6 mg. of bz. inact.-D (17); **112**: 2 mg. of bz. and 1 mg. of butyrate act.-R (17); **53A**: 0.5 mg./day relatively inact.-R (22); **79**: R.U./mg. = 6 of free cpd., < 8 of ac., 12 of pr., 17.5 of butyrate, 12 of $\frac{1}{2}$ succinate, < 6 of Na salt of $\frac{1}{2}$ succinate, 12.5 of caproate, 25 of diethyl ac., < 15 of heptoate, < 12 of bz., and < 8 of palmitate-R (16); **61**: U. = ca. 0.06-0.18 mg./kg./day-D (5,18); **52**: U. = ca. 0.5 mg.-R (3,4); **47A**: threshold dose = ca. 0.12-0.25 mg.-R (21); **146**: 0.5 mg. of free cpd. and ac. very act. but ac. more act than free cpd.-M (23).

Folliculoid: **67**: nipple stimulating-G (20); **60**: much less act. than D.C.A.-B (10).

REMARKS: Data of (1,2) incorrect according to (13).

DERIVATIVES:

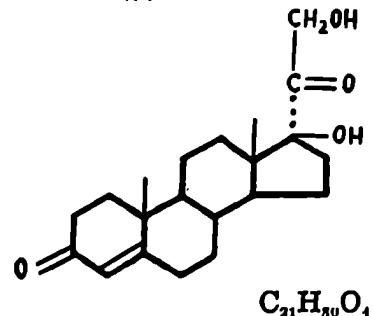
17 ² -ac.	{ 145-6°; $[\alpha]_D^{18} = +200^\circ$; $[\alpha]_{5461}^{18} = +245^\circ$ (dioxane) : (0)
	{ 153°: (6,12,16)
Butyrate	168-9°, 170-1°: (6,16)
Oleate	79-81°: (6)
Palmitate	87-93°: (6,16)
17 ² -tosylate	(15)
$\frac{1}{2}$ succinate	195-7°: (6,16)
Pr.	180-2°: (16)
Caproate	130-2°: (16)
Diet.-ac.	179-80°: (16)
Heptoate	139-41°: (16)
Bz.	201-2°: (6,16)

REFERENCES:

- | | | | | |
|-----------|------------|------------|------------|------------|
| 1. 60400 | 6. A9075 | 11. 63690 | 16. A34586 | 21. A31765 |
| 2. A33474 | 7. 72132 | 12. A19374 | 17. 75612 | 22. A34871 |
| 3. 67876 | 8. 72134 | 13. A8218 | 18. 74850 | 23. A36403 |
| 4. A1738 | 9. 83506 | 14. 78855 | 19. A38963 | |
| 5. 60294 | 10. A33485 | 15. 78850 | 20. A15203 | |

**17(α)-[1-KETO-2-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE-17(β)-OL
(Reichstein's cpd. "S", 11-desoxy-17-hydroxy-corticosterone)**

ISOLATION Ad.: (3,5,6)



STRUCTURE AND SYNTHESIS: (1,2,5,6).

M.P.: 200-5°: (6)
207-9°: (3)

PHARMACOLOGY: Corticoid: **47A**: no more act. than D.C.A.-R (4); at 2 mg. dose level act. ?-R (8); **113**: at 2 mg. dose level act. ?-R (8); **52**: U. = ca. 1 mg. of ac.-R (9); **146**: "very little or no act." -M (9).

REMARKS: Originally assigned possible structure of 17(α)-[1-hydroxy-aldoethyl]- Δ^4 -androstene-3-one-17(β)-ol but shown not to be an aldehyde (1).

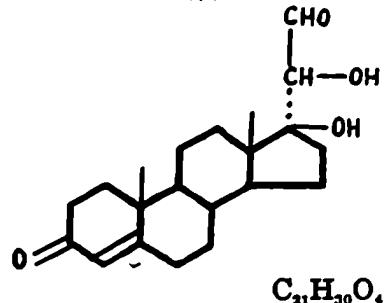
DERIVATIVES:

17²-ac. 239-41°; $[\alpha]_D^{10} = +116^\circ \pm 4^\circ$ (acetone): (3,6,7)

REFERENCES:

1. 76730
2. 75154
3. 73592
4. 80444
5. A19374
6. 79192
7. 81794
9. A58412

**17(α)-[1(β)-HYDROXY-2-ALDOETHYL]- Δ^4 -ANDROSTENE-3-ONE-17(β)-OL
 $(\Delta^4$ -pregnene-3-one-17(β),20(β)-diol-21-al)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS:

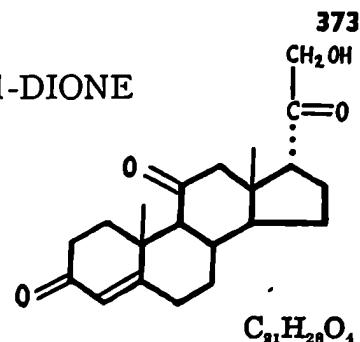
DERIVATIVES:

17¹-ac. 206-8°; $[\alpha]_D^{18} = +119^\circ \pm 3^\circ$ (dioxane): (1) 1. 79193
 Semicarb. 190°: (1)

REFERENCES:

17(α)-[1-KETO-2-HYDROXYETHYL]-Δ⁴-ANDROSTENE-3,11-DIONE
 (Kendall's cpd. "A", dehydro-corticosterone)

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ISOLATION: Ad. (2,4,6,7).

STRUCTURE AND SYNTHESIS: (1,3,4,5,7)

M.P.: 178-80°: (5,6)
 177-9.5° (u): (2,4)
 178-80° (7)

$[\alpha]_D^{25} = +258^\circ$ (alc.): (6)
 $[\alpha]_{5461}^{25} = +347^\circ$ (benzene): (2)

PHARMACOLOGY:

Corticoid: **47A**: threshold dose = 0.12 mg.-R (10); **47A**: slightly less act. than corticosterone-R (4); **53A**: 0.5 mg./day inact.-R (13); **79**: U. = 3-4 mg.-R (6); **61**: as act. as corticosterone-D (8); **119**: 0.5 mg./day act.-R (12).

Luteoid: **46**: 1 mg. inact.-Rb (16).

Anesthetic: **11**: U. = 3.5 mg.-R (11,15); **127**: 1.5 mg. inact.-Fish (15).

REMARKS:

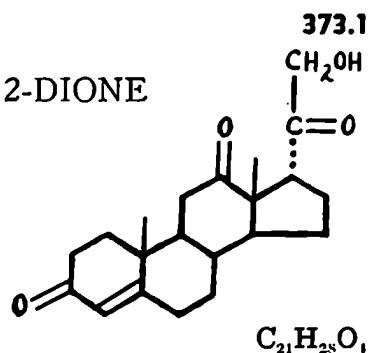
DERIVATIVES:

Ac. $\begin{cases} 179-81^\circ : \begin{cases} [\alpha]_D^{18} = +233.7^\circ; \\ [\alpha]_{5461}^{18} = +285^\circ \text{ (dioxane)} : (5,7,14) \end{cases} \\ 175-8^\circ ; [\alpha]_D^{22} = +210.7^\circ \pm 3^\circ \text{ (acetone)} : (17) \end{cases}$

REFERENCES:

1. 72170
2. 60400
3. A33474
4. 69204
5. A9075
6. A30091
7. A17374
8. 77274
9. A9077
10. A31765
11. A36744
12. A37900
13. A34971
14. 83506
15. A3S070
16. A56335
17. 84184

**17(α)-[1-KETO-2-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3,12-DIONE
[Pregnene-(4)-ol-(21)-trione-(3,12,20)]**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 180-3°: (1)

$[\alpha]_D^{22} = + 238.9^\circ \pm 3^\circ$ (dioxane): (1)

$[\alpha]_{5461}^{22} = + 298^\circ \pm 3^\circ$ (dioxane): (1)

$[\alpha]_D^{23} = + 215.1^\circ \pm 2^\circ$ (acetone): (1)

$[\alpha]_{5461}^{23} = + 265.8^\circ \pm 2^\circ$ (acetone): (1)

PHARMACOLOGY: Corticoid: **52:** 2.5 mg./day of ac. questionably act.-R (1).

REMARKS:

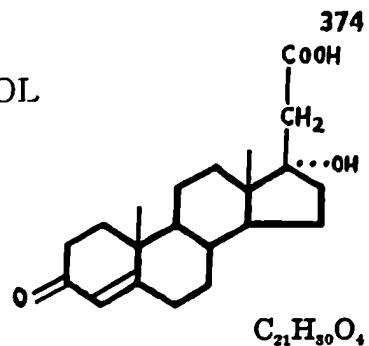
DERIVATIVES:

Ac. 182-4°; $[\alpha]_D^{14} = + 228.6^\circ \pm 3^\circ$ (acetone): (1)

REFERENCES:

1. 84187

**17(β)-CARBOXYMETHYL- Δ^4 -ANDROSTENE-3-ONE-17(α)-OL
(Δ^4 -3-keto-17(α)-hydroxy-pregnenoic acid)**



ISOLATION:

STRUCTURE AND SYNTHESIS: (1)

M.P.: 162° (u) : (1)

PHARMACOLOGY:

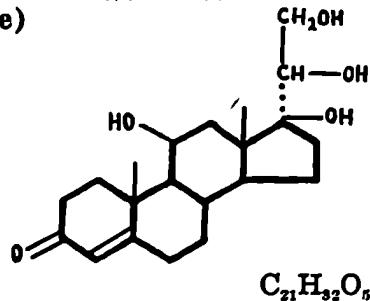
REMARKS:

DERIVATIVES:

REFERENCES:

1. 75052

**17(α)-[1(),2-DIHYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE-11(β),17(β)-DIOL
(Reichstein's cpd. "E"; Δ^4 -pregnene-11(β), 17(β), 20(),21-Tetrol-3-one)**



ISOLATION: Ad. (1,2)

STRUCTURE AND SYNTHESIS: (3,4,6,8)

M.P.: ca. 125°: (6)
120° (+H₂O): (4)
126-9°: (1)

$[\alpha]_D^{20} = +87^\circ \pm 2^\circ$ (alc.): (6)

PHARMACOLOGY: Corticoid: **112**: 2 mg. inact.-R (5); **82**: 0.5 mg./kg./day act.-D (5); **52**: 0.4 mg./day inact.-R (1,7); **56**: 1/6 as act. as corticosterone-D (7).

REMARKS:

DERIVATIVES:

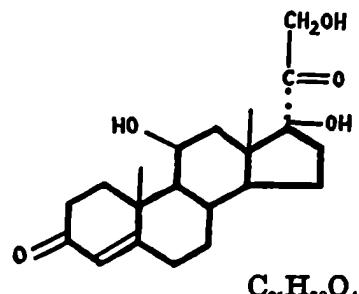
Semicarb. 280-5°:
17¹,17²-diac. 229-30°; $[\alpha]_D^{22} = +162.7^\circ \pm 2^\circ$ (acetone): (8).

REFERENCES:

- (6). 1. 34911
2. A9075
3. 63690
4. A9076
5. 75612
6. A33510
7. 72133
8. S3467

**17(α)-[1-KETO-2-HYDROXYETHYL]- Δ^4 -ANDROSTENE-3-ONE-11(β),17(β)-DIOL
(17-hydroxy-corticosterone, Kendall's cpd. "F",
Reichstein's cpd. "M")**

ISOLATION: Ad.: (1,2,3,6).



STRUCTURE AND SYNTHESIS: (3,4,5,6).

M.P.: 217-20°: (3)

210-5°: (4)

216-8°: (6)

$[\alpha]_{D}^{25} = +164^\circ$ (alc.): (4,6)

$[\alpha]_{5461}^{25} = +178^\circ \pm 2^\circ$ (alc.): (3).

PHARMACOLOGY: Corticoid: **52**: U. = 1.5 mg.-R (7); **52**: act.-R (2,9); **47A**: threshold dose = ca. 0.03-0.06 mg.-R (11); **53**: 0.5 mg./day inact.-R (12); **56**: 6 \times less act. than corticosterone and 3 \times less act. than Kendall's cpd. "E"-D (7); **61**: less act. than Kendall's cpd. "E"-D (8); **79**: U. = 1-2 mg.-R (6); **52**: 2 mg. act.-R (10); **82**: 1.25-5 mg. act.-D (10); **112**: 3 mg. act.-R (10); **113**: 5 mg./day act.-R (13); **146**: 0.5-1 mg. very act.-M (14).

REMARKS:

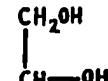
DERIVATIVES:

17 α -ac. 223.5°: (5)

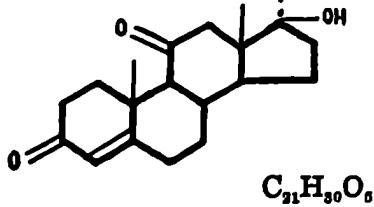
REFERENCES:

1. 68081
2. A1738
3. 72169
4. A9075
5. A9076
6. A30091
7. 72133
8. 77274
9. A9077
10. 75612
11. A31765
12. A34971
13. 83869
14. A36403

**17(α)-[1(),2-DIHYDROXYETHYL]-Δ⁴-ANDROSTENE-3,11-DIONE-17(β)-OL
(Reichstein's cpd. "U", Δ⁴-pregnene-3,11-dione-17,20,21-triol)**



ISOLATION: Ad. (1)



STRUCTURE AND SYNTHESIS: (1)

M.P.:

PHARMACOLOGY:

REMARKS: Free cpd. amorphous (1)

DERIVATIVES:

17¹,17²-diac. 252-3°; [α]_D²¹ = + 178.5° ± 2° (acetone) : (1)

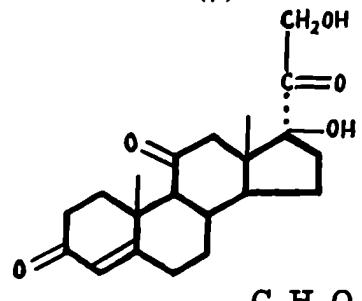
REFERENCES:

1. 83467

17(α)-[1-KETO-2-HYDROXYETHYL]-Δ⁴-ANDROSTENE-3,11-DIONE-17(β)-OL

(Reichstein's cpd. "Fa 6", Kendall's cpd. "E", Wintersteiner's
cpd. "F", 17-hydroxy-11-dehydro-corticosterone)

ISOLATION: Ad. (2,3,5,10,11,12,13,14,16)



STRUCTURE AND SYNTHESIS: (1,5,8,9,15,16)

M.P.: 207-15° (u) : (5)
213-7° : (15)
201-8° : (4)
208-17° : (16)
215-8° : (14)

$[\alpha]_{D}^{25} = + 272^\circ \pm 7^\circ$ (methanol) : (5)
 $[\alpha]_{D}^{22} = + 200^\circ$ (alc.) : (13)
 $[\alpha]_{D}^{25} = + 269^\circ$ (benzene) : (4)
 $[\alpha]_{D}^{25} = + 209^\circ$ (alc.) : (16)
 $[\alpha]_{D}^{25} = + 195^\circ$ (alc.) : (14)

PHARMACOLOGY:

Corticoid: **146**: 0.5-1 mg. very act.-M (34); **47A**: 2 mg./day act.-R (5); **47A**: threshold dose = 0.125 mg.-R (23,26); **47B**: threshold dose of free cpd. and ac. = 0.25-0.5 mg./day; much more act. than D.C.A. at high dose levels-R (23); **47C**: free cpd. and ac. inact.-R (23); Test? "little or no life maintenance effect"-R (24); **52**: 0.8 mg. inact.-R (13); **53A**: dose? inact.-R (19); **61**: up to 100 γ /kg./day inact.-D (2,16,21); **61**: dose? slightly act.-D (18); **113**: 1 mg./day act.-R (27); **61**: 350-500 γ /kg./day act.-D (17); **119**: 1 mg./day act.-R (7,29); **79**: U. = 0.5-1.0 mg.-R (14); **87**: 1 mg. more act. than 3 mg. D.C.A.-R (32); **47D**: U. = 0.4 mg.-R (33); **52**: U. = ca. 2 mg.-R (35).

Testoid: **41**: dose? inact.-C (5); **31**: 25 γ /day inact.-C (13).

Luteoid: **54**: "50 Rb. U." inact.-Rb. (5); **46**: up to 8 mg. very slight, if any act.-Rb. (22,30).

Folliculoid: **55**: vag. stratification-R (20).

Anesthetic: **11**: U. = 15 mg.-R (25,28); **127**: 3.5 mg. inact.-Fish (25).

REMARKS: Ppt. with digitonin (5).

DERIVATIVES:

17 ² -ac.	239-41°: (9,15)
2:4-dinitrophenylhydrazone	255-6° (u) : (4)
Disemicarb.	> 300°: (16)
p-nitrobz.	220-1°: (16)

REFERENCES:

1. 72170
2. 53072
3. A33483
4. 60490
5. 08643
6. 72169
7. A38216
8. A9075
9. A9076
10. A33474
11. A33481
12. 08081
13. 63690
14. A30091
15. A19372
16. A1688
17. A30013
18. 77274
19. A17828
20. A37486
21. 34911
22. A38712
23. A33857
24. 77519
25. A38070
26. A31765
27. A36742
28. A36744
29. A37900
30. A56335
31. A38071
32. A37457
33. 83871
34. A36403
35. A58412