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CHEMICALS, DRUGS, AND BIOLOGICALS

ELEVENTH EDITION

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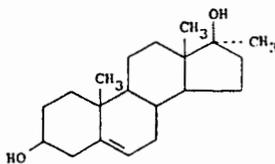
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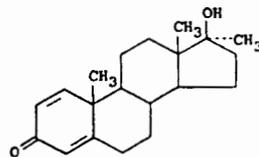
Crystals from ethyl acetate, mp 205.5-206.5°. $[\alpha]_D^{25} -73^\circ$ (alc). Insol in water. Slightly sol in some organic solvents.

Diacetate, $C_{24}H_{36}O_4$, crystals from hexane, mp 145-146°. $[\alpha]_D^{25} -59^\circ$ (c = 0.984 in alc).

Dipropionate, $C_{26}H_{40}O_4$, *Probolin*.

THERAP CAT: Anabolic.

5862. Methandrostenolone. 17-Hydroxy-17-methylandrosta-1,4-dien-3-one; 17 α -methyl-17 β -hydroxyandrosta-1,4-dien-3-one; 1-dehydro-17 α -methyltestosterone; methandienone; Danabol; Nerobol; Nabolin; Stenolon; Dianabol. $C_{20}H_{28}O_2$; mol wt 300.42. C 79.95%, H 9.39%, O 10.65%. Anabolic steroid. Prepn by microbial dehydrogenation of 17 α -methyltestosterone: Vischer *et al.*, *Helv. Chim. Acta* 38, 1502 (1955); by reduction of 17 α -methyltestosterone with selenium dioxide: Meystre *et al.*, *ibid.* 39, 734 (1956); Wettstein *et al.*, U.S. pat. 2,900,398 (1959 to Ciba).



Crystals from acetone + ether. mp 163-164°. $[\alpha]_D^{25} 0^\circ$ (c = 1.15 in chloroform). uv max: 245 nm (ϵ 15600).

THERAP CAT: Androgen.

THERAP CAT (VET): Anabolic.

5863. Methane. Marsh gas; methyl hydride. CH_4 ; mol wt 16.04. C 74.87%, H 25.13%. Widely distributed in nature. American natural gas is about 85% methane. The earth's atm contains 0.00022% by vol. Major constituent of the atm of the outer planets (Jupiter, Saturn, Uranus, Neptune), exact figures in *Landolt-Börnstein*, vol. III (Springer, 6th ed., 1952) p 59; G. P. Kuiper, *The Atmospheres of the Earth and the Planets* (University of Chicago Press, 1949). Pure carbon combines directly with pure hydrogen at temperatures above 1100° forming methane. Above 1500° amount of methane formed increases with temperature: Pring, *J. Chem. Soc.* 97, 498 (1910). Can be prepd from sodium acetate and sodium hydroxide, or from aluminum carbide and water: Matthews, *J. Am. Chem. Soc.* 21, 647 (1899); Carroll, *J. Phys. Chem.* 22, 148 (1918). Prepd commercially from natural gas or by fermentation of cellulose and sewage sludge: Cost, U.S. pat. 2,583,090 (1952 to Elliott Co.); Le Paige, de Dommartin, Fr. pat. 994,032 (1951), C.A. 51, 10836i (1957); Oswald, *Mech. Eng.* 86, 40 (1964).

Colorless, odorless, non-poisonous, flammable gas. Burns with a pale, faintly luminous flame. $d_4^{20} 0.554$ (air = 1) or 0.7168 g/liter. mp -182.6° . bp -161.4° . Crit temp -82.25° ; crit pressure 45.8 atm. Heat of combustion 978 Btu/cu ft at 25° (a kilogram of CH_4 yields 13,300 kcal). Forms explosive mixtures with air, the loudest explosions occur when one vol of methane is mixed with 10 vols of air (or 2 vols of oxygen). Air contg less than 5.53% methane no longer explodes. Air contg more than 14% methane burns without noise. Autoignition temp 650°. Soly in water at 17°: 3.5 ml/100 ml H_2O . Sol in alc, ether, other organic solvents.

USE: Constituent of illuminating and cooking gas, in the manuf of hydrogen, hydrogen cyanide, ammonia, acetylene, formaldehyde, in organic syntheses. *Caution:* Simple asphyxiant.

5864. Methanearsonic Acid. *Methylarsonic acid*; methylarsinic acid; monomethylarsinic acid. CH_3AsO_3 ; mol wt 139.96. C 8.58%, H 3.60%, As 53.53%, O 34.30%. $CH_3AsO(OH)_2$. Prepd from sodium arsenite and methyl iodide:

Quick, Adams, *J. Am. Chem. Soc.* 44, 809 (1922) sodium salt is easily prepd by treating sodium dimethyl sulfate at 85°: Uhlinger, Cook, *Ind. Eng. Chem.* 105 (1919). Other routes are by the reaction of methyl iodide with sodium arsenate under pressure: Miller, U.S. pat. 2,442,372 (1948); by the reaction of dimethyl sulfate with a solution of arsenic trioxide in sodium hydroxide: Schwerdtle, U.S. pat. 2,889,347 (1959). Acute toxicity: Gaines, R. E. Linder, *Fundam. Appl. Toxicol.* 7, 103 (1975). Monoclinic, spear-shaped plates from abs alcohol. Ant acid taste. mp 161°. Strong dibasic acid. Freely sol in water; sol in alcohol.

Monosodium salt, CH_3AsNaO_3 , *monosodium methylarsonate*, MSMA, Ansar 170, Ansar 529, Buena Vista, Trans-vert, Weed-E-Rad 120, Weed Hoc. LD₅₀ in adult female rats (mg/kg): 1105, 1059 orally (Gaines).

Disodium salt, $CH_3AsNa_2O_3$, *disodium methylarsonate*, DSMA, Ansar 184, Ansar 8100, Arrhenal, Arsynal, Cacodyl New, Clout, Crab-E-Rad, Dalgranular, Neo-Arsycodile, Sodar, Stenosine, Tonarsin, E-Rad 360, Weedone Crabgrass Killer Granular. Crystals contg 5 H_2O or 6 H_2O . One gram dissolves in one ml water; slightly sol in alcohol. LD₅₀ in adult female rats (mg/kg): 928, 821 orally (Gaines). Disodium methylarsonate combined with an equal amount of mercury salicylate is called *Enesol*; white powder; sol in water.

USE: Herbicide.

5865. Methanesulfonic Acid. Methylsulfonic acid. CH_3SO_3H ; mol wt 96.10. C 12.50%, H 4.19%, O 49.33, 33.37%. CH_3SO_3OH . Prepd from sulfur trioxide and methane: Snyder, Grosse, U.S. pat. 2,493,038 (1950 to E. I. du Pont de Nemours & Co.); by oxidation of dimethyl disulfide: J. Wolff, U.S. pat. 2,697,722 (1954 to Standard Oil of Indiana); Proell *et al.*, *Ind. Eng. Chem.* 40, 1129 (1948). preps and chemistry: Suter, *The Organic Chemistry of Sulfur* (Wiley, New York, 1944).

Solid. $d_4^{20} 1.4812$. mp 20°. bp₁₀ 167°; bp₁ 122°. 26-28° in wt %: hexane, 0; methylcyclopentane, 0; benzene, 1.50; toluene, 0.38; o-chlorotoluene, 0.23; ethyl acetate, 0.47. Thermally stable at moderately elevated temperatures. Hydrolyzed by boiling water or hot aq alkali. Corrosive to iron, steel, brass, copper, lead.

Ethyl ester see Ethyl Methanesulfonate.

Methyl ester see Methyl Methanesulfonate.

USE: As catalyst in polymerization, alkylation and acylation reactions; as a solvent. *Caution:* Strongly corrosive.

5866. Methanesulfonyl Chloride. CH_3SO_2Cl ; mol wt 114.55. C 10.48%, H 2.64%, Cl 30.95%, O 27.99%. CH_3SO_2Cl . Prepd from methanesulfonic acid and thionyl chloride: Hearst, Noller, *Org. Syn.*, coll. vol. IV (1963).

Liquid. $d_4^{20} 1.4805$. bp₇₆₀ 161°; bp₁₈ 62°. $n_D^{20} 1.4511$. Slightly insol in water; sol in alcohol, ether.

5867. Methanethiol. Methyl mercaptan; mercaptane; thiomethyl alcohol; methyl sulfhydrylate. CH_3SH ; mol wt 48.11. C 24.96%, H 8.38%, S 66.65%. CH_3SH . Occurs as "sour" gas of W. Texas, in coal tar, and in petroleum condensates. Isolated from roots of *Raphanus sativus*. Produces the intestinal tract by the action of anaerobic bacteria on albumin. Evolved from *Penicillium brevicaulis* cultures containing disulfides. Prepn from sodium methylsulfate and KHS: Klason, *Ber.* 20, 3409 (1887); Arnold, *Ber.* 54, 2236 (1921); catalytically from methanol and hydrogen sulfide: Kramer, Reid, *J. Am. Chem. Soc.* 43, 880 (1921); from methyl chloride and sodium hydrosulfide: Scott, *Ind. Eng. Chem.* 47, 876 (1955). Toxicity data: *Handbook of Toxicology* vol. 1, W. S. Spector, Ed. (Saunders, Philadelphia, 1956) pp 344-345. Review on occurrence, preparation, properties and reactions: E. E. Reid, *Organic Chemistry of Sulfur* vol. I (Chemical Publishing Co., New York, 1958) pp 15-261.

Flammable gas; odor of rotten cabbage. mp -123° . 5.95°; $d_4^{20} 0.8665$; $d_4^{25} 0.9600$. Critical temp 196.8°. Critical pressure 71.4 atm. Heat capacity (solid at 14.97-146.57°K): 0.773-17.47 cal/deg/mole; (liq at 154.16-271.06°K): 21.13 cal/deg/mole, Russell *et al.*, *J. Am. Chem. Soc.* 64, 2113 (1942). Azeotrope with isobutane (14.9% methanethiol).