

Dodecyltrimethylammonium chloride [112-00-5] M 263.9, m 246°(dec). Dissolved in MeOH, treated with active charcoal, filtered and dried *in vacuo* [Waldenburg *J Phys Chem* 88 1655 1984], or recrystd several times from 10% EtOH in acetone. Also repeatedly crystd from EtOH/ether or MeOH. [Cella et al. *J Am Chem Soc* 74 2062 1952.]

Dulcitol [608-66-2] M 182.2, m 188-189°, b 276-280°/1.1mm. Crystd from water by addition of EtOH.

Duroquinone (tetramethylbenzoquinone) [527-17-3] M 164.2, m 110-111°. Crystd from 95% EtOH. Dried under vacuum.

α -Ecdyson [3604-87-3] M 464.7, m 239-242°, 242°, $[\alpha]_D^{20} +72^\circ$ (c 1, EtOH). Recrystd from tetrahydrofuran-pet ether, and from H₂O as a hydrate. It has been purified by chromatography on Al₂O₃ and elution with EtOAc-MeOH. It has λ_{\max} at 242nm (ϵ 12.400). Its *acetate* has m 214-216° from EtOAc-pet ether, and the *2,4-dinitrophenylhydrazone* has m 170-175° (dec) from EtOAc. [Karlson and Hoffmeister *Justus Liebigs Ann Chem* 662 1 1963; Karlson *Pure Appl Chem* 14 75 1967.]

β -Ecdyson (β -echdysterone) [5289-74-7] M 480.7, m 245-247°, $[\alpha]_D^{20} +66^\circ$ (c 1, MeOH). Crystd from water or tetrahydrofuran/pet ether.

Echinenone [432-68-8] M 550.8, m 178-179°, $A_{1\text{cm}}^{1\%}(\lambda_{\max})$ 2160 (458nm) in pet ether. Purified by chromatography on partially deactivated alumina or magnesia, or by using a thin layer of silica gel G with 4:1 cyclohexane/diethyl ether as the developing solvent. Stored in the dark at -20°.

Eicosane [112-95-8] M 282.6, m 36-37°, b 205°/15mm, $d^{36.7}$ 0.7779, n^{40} 1.43453. Crystd from EtOH.

Elaidic (*trans*-oleic) acid [112-79-8] M 282.5, m 44.5°, pK^{25} 4.9. Crystd from acetic acid, then EtOH.

Ellagic acid (2H₂O) [476-66-4] M 338.2, m >360°, $pK_{\text{Est}(1)} \sim 8$, $pK_{\text{Est}(2)} \sim 11$. Crystd from pyridine.

Elymoclavine (8,9-didehydro-6-methylergoline-8-methanol) [548-43-6] M 254.3, m 249-253°(dec), $[\alpha]_D^{20} -59^\circ$ (c 1, EtOH). Crystd from MeOH.

Embonic acid (Pamoic acid, 4,4'-methylene bis[3-hydroxy-2-naphthalenecarboxylic acid]) [130-85-8] M 388.4, m 295°, >300°, $pK_{\text{Est}(1)} \sim 2.2$, $pK_{\text{Est}(2)} \sim 13.2$. Forms crystals from dilute pyridine which decomposition above 280° without melting. It is almost insoluble in H₂O, EtOH, Et₂O, *C₆H₆, CH₃CO₂H, sparingly soluble in CHCl₃ but soluble in nitrobenzene, pyridine and alkalis [Barber and Gaimster *J Appl Chem (London)* 2 565 1952]. Used for making salts of organic bases.

Emetine hydrochloride hydrate [316-42-7] M 553.6 + aq, m 235-240°, 235-250°, 240-250°, 248-250° (depending on H₂O content), $[\alpha]_D^{20} -49.2^\circ$ (free base, c 4, CHCl₃), +18° (c 6, H₂O, dry salt), pK_1 5.77, pK_2 6.64. It crystallises from MeOH-Et₂O, MeOH or Et₂O-EtOAc. The *free base* has m 104-105°, and the (*-*)-*phenyl thiourea derivative* has m 220-221° [from EtOAc-pet ether, $[\alpha]_D^{25} -29.3^\circ$ (CHCl₃)]. IR: 3413 (OH) and 2611 (NH⁺) cm⁻¹; UV λ_{\max} 230nm (ϵ 16 200) and 282nm (ϵ 6 890) [Brossi et al. *Helv Chim Acta* 42 1515 1959; Barash et al. *J Chem Soc* 3530 1959].

Emodine (1,3,8-trihydroxy-6-methyl-9,10-anthracenedione, archin) [518-82-1] M 270.2, m 253-257°, 255-256°, 256-257°, 262°, 264° (phenolic pKs 7-10). Forms orange needles from EtOH, Et₂O, *C₆H₆, toluene or pyridine. It sublimes above 200° at 12mm. [Tutin and Clewer *J Chem*

Soc 99 946 1911; IR: Bloom et al. *J Chem Soc* 178 1959; UV: Birkinshaw *Biochem J* 59 495 1955; Raistrick *Biochem J* 34 159 1940.]

1*R*,2*S*-(-)Ephedrine [299-42-3] *M* 165.2, *m* 40°, *b* 225°, $[\alpha]_{546}^{20}$ -47° and $[\alpha]_{\text{D}}^{20}$ -40° (c 5, 2.2M HCl), pK^{25} 9.57. See (-)-ephedrine (1*R*,2*S*-2-methylamino-1-phenylpropanol) on p. 533 in Chapter 6.

(-)-Ephedrine hydrochloride [50-98-6] *M* 201.7, *m* 218°, $[\alpha]_{546}^{20}$ -48° (c 5, 2M HCl). Crystd from water.

Epichlorohydrin [106-89-8] *M* 92.5, *b* 115.5°, *n* 1.438, *d* 1.180. Distd at atmospheric pressure, heated on a steam bath with one-quarter its weight of CaO, then decanted and fractionally distd.

***R*(-)-Epinephrine (adrenalin)** [51-43-4] *M* 183.2, *m* 215°(dec), $[\alpha]_{546}^{20}$ -61° (c 5, 0.5M HCl), pK_1^{25} 8.75, pK_2^{25} 9.89, pK_3^{25} ~13. Dissolved in dilute aqueous acid, then pptd by addn of dilute aqueous ammonia or alkali carbonates. (Epinephrine readily oxidises in neutral alkaline soln. This can be diminished if a little sulfite is added).

1,2-Epoxybutane [106-88-7] *M* 72.1, *b* 66.4-66.6°, *d* 0.837, *n* 1.3841. Dried with CaSO₄, and fractionally distd through a long (126cm) glass helices-packed column. The first fraction contains a water azeotrope.

(+)-Equilenine [517-09-9] *M* 266.3, *m* 258-259°, $[\alpha]_{\text{D}}^{16}$ +87° (c 7.1, H₂O). Crystd from EtOH and dried in a vacuum.

Ergocornine [564-36-3] *M* 561.7, *m* 182-184°, $[\alpha]_{\text{D}}^{20}$ -176° (c 0.5, CHCl₃). Crystd with solvent of crystn from MeOH.

Ergocristine [511-08-0] *M* 573.7, *m* 165-170°, $[\alpha]_{\text{D}}^{20}$ -183° (c 0.5, CHCl₃). Crystd with 2 moles of solvent of crystn, from *benzene.

Ergocryptine [511-09-1] *M* 575.7, *m* 212-214°, $[\alpha]_{\text{D}}^{20}$ -180° (c 0.5, CHCl₃). Crystd with solvent of crystn, from acetone, *benzene or methanol.

Ergosterol [57-87-4] *M* 396.7, *m* 165-166°, $[\alpha]_{546}^{20}$ -171° (in CHCl₃). Crystd from ethyl acetate, then from ethylene dichloride.

Ergotamine [113-15-5] *M* 581.6, *m* 212-214°(dec), $[\alpha]_{\text{D}}^{20}$ -160° (c 0.5, CHCl₃), pK^{25} 6.40. Crystd from *benzene, then dried by prolonged heating in high vacuum. Very *hygroscopic*.

Ergotamine tartrate [379-79-3] *M* 657.1, *m* 203°(dec). Crystd from MeOH.

Erucic acid (cis-13-docosenoic acid) [112-86-7] *M* 338.6, *m* 33.8°, *b* 358°/400mm, pK_{Est} ~4.9. Crystd from MeOH.

meso-Erythritol [149-32-6] *M* 122.1, *m* 122°. Crystd from distd water and dried at 60° in a vac oven.

Erythrityl tetranitrate [7297-25-8] *M* 302.1, *m* 61°. Crystd from EtOH.

β-Erythroidine [466-81-9] *M* 273.3, $[\alpha]_{\text{D}}^{20}$ +89° (H₂O). Crystd from EtOH.

D-Erythronic acid (3*R*-3,4-dihydroxyfuran-2-one) [15667-21-7] *M* 118.1, *m* 98-100°, 103-104°, 104-105°, 105°, $[\alpha]_{\text{D}}^{20}$ -73.2° (c 0.5, H₂O), $[\alpha]_{546}^{20}$ -87.6° (c 4, H₂O). Recrystd from EtOAc (20 parts) or isoPrOH (3 parts). [Baker and MacDonald *J Am Chem Soc* 82 230 1960; Glattfeld and

Forbrich *J Am Chem Soc* **56** 1209 1934; Weidenhagen and Wegner *Chem Ber* **72** 2010 1939, Musich and Rapoport *J Am Chem Soc* **100** 4865 1978.]

Esculetin (cichorigenin, 6,7-dihydroxycoumarin) [305-01-1] **M 178.2, m 272-275° (dec), 274° (dec), $pK_{Est(1)} \sim 8.7$, $pK_{Est(2)} \sim 12.4$.** Forms prisms from AcOH or aq EtOH and provides leaflets on sublimation in a vacuum. [Sethna and Shah *Chem Rev*; Merz *Arch Pharm (Weinheim Ger)* **270** 486 1932.] *Esculin (the 6-glucoside)* has **m 215° (dec), $[\alpha]_D^{20} -41^\circ$ (c 5, pyridine).**

Eserine (Physostigmine, Physostol, [(3a*S*-*cis*)-1,2,3,3a,8,8a-hexahydro-1,3a,8-trimethyl-pyrrolo[2,3-*b*]indol-5-ol methylcarbamate ester] [57-47-6] **M 275.4, m 102-104°, 105-106°, $[\alpha]_D^{17} -67^\circ$ (c 1.3, CHCl₃), $[\alpha]_D^{25} -120^\circ$ (*C₆H₆), $pK_1^{15} 1.96$, $pK_2^{15} 8.08$.** Recrystallises from Et₂O or *C₆H₆ and forms an unstable low melting form **m 86-87°** [Harley-Mason and Jackson *J Chem Soc* 3651 1954; Wijnberg and Speckamp *Tetrahedron* **34** 2399 1978].

1,3,5-Estratrien-3-ol-17-one (Estrone, Folliculin) [53-16-7] **M 270.4, m 260-261°, polymorphic also m 254° and 256°, $[\alpha]_{546}^{20} +198^\circ$ (c 1, dioxane), $pK^{25} 10.91$.** Crystd from EtOH.

1,3,5-Estratrien-3 β ,16a,17 β -triol (Estriol) [50-27-1] **M 288.4, m 283°, $[\alpha]_{546}^{20} +66^\circ$ (c 1, dioxane).** Crystd from EtOH/ethyl acetate.

Ethane [74-84-0] **M 30.1, f -172°, b -88°, $d_4^0 1.0493$ (air = 1).** Ethylene can be removed by passing the gas through a sintered-glass disc into fuming H₂SO₄ then slowly through a column of charcoal satd with bromine. Bromine and HBr were removed by passage through firebrick coated with *N,N*-dimethyl-*p*-toluidine. The ethane was also passed over KOH pellets (to remove CO₂) and dried with Mg(ClO₄)₂. Further purification was by several distns of liquified ethane, using a condensing temperature of -195°. Yang and Gant [*J Phys Chem* **65** 1861 1961] treated ethane by standing it for 24h at room temperature in a steel bomb containing activated charcoal treated with bromine. They then immersed the bomb in a Dry-ice/acetone bath and transferred the ethane to an activated charcoal trap cooled in liquid nitrogen. (The charcoal had previously been degassed by pumping for 24h at 450°.) By allowing the trap to warm slowly, the ethane was distd, retaining only the middle third. Removal of methane was achieved using Linde type 13X molecular sieves (previously degassed by pumping for 24h at 450°) in a trap which, after cooling in Dry-ice/acetone, was satd with ethane. After pumping for 10min, the ethane was recovered by warming the trap to room temperature. (The final gas contained less than 10⁻⁴ mole % of either ethylene or methane).

Ethanesulfonyl chloride [594-44-5] **M 128.6, b 55°/9mm, 62°/12mm, 74°/19mm, 76-79°/22mm, 95-98°/50mm, 177°/760mm, $d_4^{20} 1.357$, $n_D^{20} 1.4539$.** Purified by repeated distn to remove HCl formed from hydrolysis. **Fuming, corrosive liquid, handle in a good fumehood.** It is hydrolysed by aq N NaOH at room temperature and is best stored in aliquots in sealed ampules under N₂. [Davies and Dick *J Chem Soc* 484 1932; Klamann and Drahowzal *Monatsh Chem* **83** 463 1952; Saunders et al. *Biochem J* **36** 372 1942.]

Ethanethiol (ethyl mercaptan) [75-08-1] **M 62.1, b 32.9°/704mm, $d^{52} 0.83147$, $pK^{25} 10.61$.** Dissolved in aqueous 20% NaOH, extracted with a small amount of *benzene and then steam distd until clear. After cooling, the alkaline soln was acidified slightly with 15% H₂SO₄ and the thiol was distd off, dried with CaSO₄, CaCl₂ or 4A molecular sieves, and fractionally distd under nitrogen [Ellis and Reid *J Am Chem Soc* **54** 1674 1932].

Ethanol [64-17-5] **M 46.1, b 78.3°, $d^{15} 0.79360$, $d^5 0.78506$, n 1.36139, $pK^{25} 15.93$.** Usual impurities of fermentation alcohol are fusel oils (mainly higher alcohols, especially pentanols), aldehydes, esters, ketones and water. With synthetic alcohol, likely impurities are water, aldehydes, aliphatic esters, acetone and diethyl ether. Traces of *benzene are present in ethanol that has been dehydrated by azeotropic distillation with *benzene. Anhydrous ethanol is very *hygroscopic*. Water (down to 0.05%) can be detected by formation of a voluminous ppt when aluminium ethoxide in *benzene is added to a test portion, Rectified

spirit (95% ethanol) is converted to *absolute* (99.5%) ethanol by refluxing with freshly ignited CaO (250g/L) for 6h, standing overnight and distilling with precautions to exclude moisture.

Numerous methods are available for further drying of *absolute* ethanol for making "Super dry ethanol". Lund and Bjerrum [*Chem Ber* **64** 210 1931] used reaction with magnesium ethoxide, prepared by placing 5g of clean dry magnesium turnings and 0.5g of iodine (or a few drops of CCl₄), to activate the Mg, in a 2L flask, followed by 50-75 mL of *absolute* ethanol, and warming the mixture until a vigorous reaction occurs. When this subsides, heating is continued until all the magnesium is converted to magnesium ethoxide. Up to 1L of ethanol is added and, after an hour's reflux, it is distd off. The water content should be below 0.05%. Walden, Ulich and Laun [*Z Phys Chem* **114** 275 1925] used amalgamated aluminium chips, prepared by degreasing aluminium chips (by washing with Et₂O and drying in a vac to remove grease from machining the Al), treating with alkali until hydrogen was vigorously evolved, washing with H₂O until the washings were weakly alkaline and then stirring with 1% HgCl₂ soln. After 2min, the chips were washed quickly with H₂O, then alcohol, then ether, and dried with filter paper. (The amalgam became warm.) These chips were added to the ethanol, which was then gently warmed for several hours until evolution of hydrogen ceased. The alcohol was distd and aspirated for some time with pure dry air. Smith [*J Chem Soc* 1288 1927] reacted 1L of *absolute* ethanol in a 2L flask with 7g of clean dry sodium, and added 25g of pure ethyl succinate 27g of pure ethyl phthalate was an alternative), and refluxed the mixture for 2h in a system protected from moisture, and then distd the ethanol. A modification used 40g of ethyl formate, instead, so that sodium formate separated out and, during reflux, the excess of ethyl formate decomposed to CO and ethanol.

Drying agents suitable for use with ethanol include Linde type 4A molecular sieves, calcium metal, and CaH₂. The calcium hydride (2g) was crushed to a powder and dissolved in 100mL *absolute* ethanol by gently boiling. About 70mL of the ethanol were distd off to remove any dissolved gases before the remainder was poured into 1L of *ca* 99.9% ethanol in a still, where it was boiled under reflux for 20h, while a slow stream of pure, dry hydrogen (better use nitrogen or Ar) was passed through. It was then distd [Rüber *Z Elektrochem* **29** 334 1923]. If calcium was used for drying, about ten times the theoretical amount should be taken, and traces of ammonia (from some calcium nitride in the Ca metal) would be removed by passing dry air into the vapour during reflux.

Ethanol can be freed from traces of basic materials by distn from a little 2,4,6-trinitrobenzoic acid or sulfanilic acid. *Benzene can be removed by fractional distn after adding a little water (the *benzene/water/ethanol azeotrope distils at 64.9°); the alcohol is then redried using one of the methods described above. Alternatively, careful fractional distn can separate *benzene as the *benzene/ethanol azeotrope (b 68.2°). Aldehydes can be removed from ethanol by digesting with 8-10g of dissolved KOH and 5-10g of aluminium or zinc per L, followed by distn. Another method is to heat under reflux with KOH (20g/L) and AgNO₃ (10g/L) or to add 2.5-3g of lead acetate in 5mL of water to 1L of ethanol, followed (slowly and without stirring) by 5g of KOH in 25mL of ethanol: after 1hr the flask is shaken thoroughly, then set aside overnight before filtering and distilling. The residual water can be removed by standing the distillate over activated aluminium amalgam for 1 week, then filtering and distilling. Distn of ethanol from Raney nickel eliminates catalyst poisons.

Other purification procedures include pre-treatment with conc H₂SO₄ (3mL/L) to eliminate amines, and with KMnO₄ to oxidise aldehydes, followed by refluxing with KOH to resinify aldehydes, and distilling to remove traces of H₃PO₄ and other acidic impurities after passage through silica gel, and drying over CaSO₄. Water can be removed by azeotropic distn with dichloromethane (azeotrope boils at 38.1° and contains 1.8% water) or 2,2,4-trimethylpentane.

Rapid purification: Place degreased Mg turnings (grease from machining the turnings is removed by washing with dry EtOH then Et₂O, and drying in a vac) (5g) in a dry 2L round bottomed flask fitted with a reflux condenser (protect from air with a drying tube filled with CaCl₂ or KOH pellets) and flush with dry N₂. Then add iodine crystals (0.5g) and gently warm the flask until iodine vapour is formed and coats the turnings. Cool, then add EtOH (50mL) and carefully heat to reflux until the iodine disappears. Cool again then add more EtOH (to 1L) and reflux under N₂ for several hours. Distil and store over 3A molecular sieves (pre-heated at 300°-350° for several hours and cooled under dry N₂ or argon).

S-Ethionine [13073-35-3] M 163.2, m 282°(dec), [α]_D²⁵ +23.7° (in 5M HCl), pK²⁵ 9.02 (for RS). Likely impurities are N-acetyl-(R and S)-ethionine, S-methionine, and R-ethionine. Crystd from water by adding 4 volumes of EtOH.

Ethoxycarbonyl isocyanate [19617-43-7] M 115.1, b 51-55°/13mm, 56°/18mm, d_4^{20} 1.15. Fractionally distilled. [*J Heterocycl Chem* 5 837 1968.]

Ethoxycarbonyl isothiocyanate [16182-04-0] M 131.5, b 43°/14mm, 51-55°/13mm, 56°/18mm, d_4^{20} 1.12. Fractionally distd through a short column. It also distils at 83°/30mm with some decomposition liberating CO₂ and sulfurous gases, best distil below 20mm vacuum. [*J Chem Soc* 93 697 1908; 1340, 1948; *J Heterocycl Chem* 5 837 1968.]

3-Ethoxy-N,N-diethylaniline [1846-92-2] M 193.3, b 141-142°/15mm pK_{Est} ~6.1. Refluxed for 3h with acetic anhydride, then fractionally distilled under reduced pressure.

2-Ethoxyethanol [110-80-5] M 90.1, b 134.8°, d 0.931, n 1.40751. Dried with CaSO₄ or K₂CO₃, filtered and fractionally distd. Peroxides can be removed by refluxing with anhydrous SnCl₂ or by filtration under slight pressure through a column of activated alumina.

2-Ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) [16357-59-8] M 247.3, m 63.5-65°, 66-67°. Dissolve ~180g in CHCl₃, evap to dryness under vac. Add dry Et₂O (20mL) when a white solid separates on standing. Set aside for a few hours, collect solid, wash thoroughly with cold Et₂O and dry in vac (~140g, m 63.5-65°). A further crop of solid (~25g) is obtained from the filtrate on standing overnight. [Fieser and Fieser *Reagents for Organic Synthesis* 2 191 1969; Belleau et al. *J Am Chem Soc* 90 823 1968 and 90 1651 1968.]

2-Ethoxyethyl ether [bis-(2-ethoxyethyl) ether] [112-36-7] M 162.2, b 76°/32mm, d 0.910, n 1.412. See diethyleneglycol diethyl ether on p. 203.

2-Ethoxyethyl methacrylate [2370-63-0] M 158.2, b 91-93°/35mm, d 0.965, n 1.429. Purified as described under methyl methacrylate.

1-Ethoxynaphthalene [5328-01-8] M 172.2, b 136-138°/14mm, 282°/760mm, d 1.061, n 1.604. Fractionally distd (twice) under a vacuum, then dried with, and distd under a vacuum from, sodium.

2-Ethoxynaphthalene [93-18-5] M 172.2, m 35.6-36.0°, b 142-143°/12mm. Crystd from pet ether. Dried under vacuum or distd in a vacuum.

Ethyl acetimidate [1000-84-6] M 87.1, b 92-95°/atm, 89.7-90°/765mm, d 0.8671, n 1.4025, pK_{Est} ~5.5. It is best to prepare it freshly from the *hydrochloride* (see below). Dissolve the hydrochloride (123.5g) by adding it slowly to an ice-cold mixt of H₂O (500mL), K₂CO₃ (276g) and Et₂O (200mL) and stirring rapidly. The Et₂O layer was separated, the aq layer was extd with Et₂O (100mL), the combined Et₂O layers were dried (MgSO₄), evapd and the residual oil distd through a glass helices packed column (70x1.2cm). The yield was 19g (22%). [Glickman and Cope *J Am Chem Soc* 67 1020 1945; Chaplin and Hunter *J Chem Soc* 1118 1937; *Methods Enzymol* 25 585 1972.]

Ethyl acetimidate hydrochloride [2208-07-3] M 123.6, m 98-100°(dec), 110-115° (dec), 112-113°(dec), m 112-114°(dec), pK_{Est} ~5.5. Recrystd by dissolving in the minimum volume of super dry EtOH and addition of dry Et₂O or from dry Et₂O. Dry in vacuum and store in a vacuum desiccator with P₂O₅. Alternatively it could be crystd from EtOH (containing a couple of drops of ethanolic HCl) and adding dry Et₂O. Filter and dry in a vac desiccator over H₂SO₄ and NaOH. [Pinner *Chem Ber* 16 1654 1883.] [Glickman and Cope *J Am Chem Soc* 67 1020 1945; Chaplin and Hunter *J Chem Soc* 1118 1937; McElvain and Schroeder *J Am Chem Soc* 71 40 1949; McElvain and Tate *J Am Chem Soc* 73 2233 1951; *Methods Enzymol* 25 585 1972.]

Ethyl acetate [141-78-6] M 88.1, b 77.1°, d 0.9003, n 1.37239, n_D^{25} 1.36979, pK^{25} -6.93 (aq H₂SO₄). The commonest impurities are water, EtOH and acetic acid. These can be removed by washing with aqueous 5% Na₂CO₃, then with saturated aqueous CaCl₂ or NaCl, and drying with K₂CO₃, CaSO₄ or MgSO₄. More efficient drying is achieved if the solvent is further dried with P₂O₅, CaH₂ or molecular sieves before

distn. CaO has also been used. Alternatively, ethanol can be converted to ethyl acetate by refluxing with acetic anhydride (*ca* 1mL per 10mL of ester); the liquid is then fractionally distd, dried with K_2CO_3 and redistd.

Rapid purification: Distil, dry over K_2CO_3 , distil again and store over 4A molecular sieves.

Ethyl acetoacetate [141-97-9] M 130.1, b 71°/12mm, 100°/80mm, d 1.026, n 1.419, pK²⁵ 10.68. Shaken with small amounts of saturated aqueous $NaHCO_3$ (until no further effervescence), then with water. Dried with $MgSO_4$ or $CaCl_2$. Distd under reduced pressure.

Ethyl acrylate [140-88-5] M 100.1, b 20°/40mm, 99.5°/atm, d 0.922, n 1.406. Washed repeatedly with aqueous NaOH until free from inhibitors such as hydroquinone, then washed with saturated aqueous $CaCl_2$ and distd under reduced pressure. Hydroquinone should be added if the ethyl acrylate is to be stored for extended periods. **LACHRYMATORY.**

Ethylamine [75-04-7] M 45.1, b 16.6°/760mm, d 1.3663, pK²⁰ 10.79. Condensed in an all-glass apparatus cooled by circulating ice-water, and stored with KOH pellets below 0°.

Ethylamine hydrochloride [557-66-4] M 81.5, m 109-110°. Crystd from absolute EtOH or MeOH/ $CHCl_3$.

Ethyl *o*-aminobenzoate [94-09-7] M 165.2, m 92°, pK²⁵ 2.39. Crystd from EtOH/ H_2O and air dried.

***p*-Ethylaniline** [589-16-2] M 121.2, b 88°/8mm, d 0.975, n 1.554, pK²⁵ 5.00. Dissolved in *benzene, then acetylated. The acetyl derivative was recrystallised from *benzene/pet ether, and hydrolysed by refluxing 50g with 500mL of water and 115mL of conc H_2SO_4 until the soln becomes clear. The amine sulfate was isolated, suspended in water and solid KOH was added to regenerate the free base, which was separated, dried and distd from zinc dust under a vacuum [Berliner and Berliner *J Am Chem Soc* 76 6179 1954].

Ethylbenzene [100-41-6] M 106.2, b 136.2°, d 0.867, n 1.49594, n²⁵ 1.49330. Shaken with cold conc H_2SO_4 until a fresh portion of acid remained colourless, then washed with aqueous 10% NaOH or $NaHCO_3$, followed by distilled water until neutral. Dried with $MgSO_4$ or $CaSO_4$, then dried further with, and distd from, sodium, sodium hydride or CaH_2 . Can also be dried by passing through silica gel. Sulfur-containing impurities have been removed by prolonged shaking with mercury. Also purified by fractional freezing.

Ethyl benzoate [93-89-0] M 150.2, b 98°/19mm, 212.4°/760mm, d 1.046, n¹⁵ 1.5074, n²⁵ 1.5043, pK -7.37 (aq H_2SO_4). Washed with aq 5% Na_2CO_3 , then satd $CaCl_2$, dried with $CaSO_4$ and distd under reduced pressure.

Ethyl bis-(2,4-dinitrophenyl)acetate [5833-18-1] M 358.3, m 150-153°. Crystd from toluene as pale yellow crystals.

Ethyl bixin [6895-43-8] M 436.6, m 138°. Crystd from EtOH.

Ethyl bromide [74-96-4] M 109.0, b 0°/165mm, 38°/745mm, d 1.460, n 1.4241. The main impurities are usually EtOH and water, with both of which it forms azeotropes. Ethanol and unsaturated compounds can be removed by washing with conc H_2SO_4 until no further coloration is produced. The ethyl bromide is then washed with water, aq Na_2CO_3 , and water again, then dried with $CaCl_2$, $MgSO_4$ or CaH_2 , and distd. from P_2O_5 . Olefinic impurities can also be removed by storing the ethyl bromide in daylight with elementary bromine, later removing the free bromine by extraction with dil aq Na_2SO_3 , drying the ethyl bromide with $CaCl_2$ and fractionally distilling. Alternatively, unsaturated compounds can be removed by bubbling oxygen containing *ca* 5% ozone through the liquid for an hour, then washing with aqueous Na_2SO_3 to hydrolyse ozonides and remove hydrolysis products, followed by drying and distn.

Ethyl bromoacetate [105-36-2] M 167.0, b 158-158.5°/758mm, d 1.50, n 1.450. Washed with saturated aqueous Na₂CO₃ (three times), 50% aq CaCl₂ (three times) and saturated aqueous NaCl (twice). Dried with MgSO₄, CaCl₂ or CaCO₃, and distd. **LACHRYMATORY.**

Ethyl 2-(bromomethyl)acrylate [17435-72-2] M 193.1, b 38°/0.8mm, d 1.398, n 1.479. If it contains some free acid, add H₂O, cool, and neutralise with NaHCO₃ until evolution of CO₂ ceases. Extract the mixt with Et₂O (3x) and dry combined extracts (Na₂SO₄, 3h). Evap Et₂O and dist ester collecting fraction b 39-40°/0.9mm and check spectra. [Prep and NMR: Ramarajan et al. *Org Synth Coll Vol VII* 211 1990.]

Ethyl α-bromopropionate [535-11-5] M 181.0, b 69-70°/25mm, d 1.39, n 1.447. Washed with saturated aqueous Na₂CO₃ (three times), 50% aq CaCl₂ (three times) and saturated aqueous NaCl (twice). Dried with MgSO₄, CaCl₂ or CaCO₃, and distd. **LACHRYMATORY.**

Ethyl bromopyruvate [70-23-5] M 195.0, b 47°/0.5mm, 71-73°/5mm, 87°/9mm, 89-104°/14mm, d₄²⁰ 1.561, n_D²⁰ 1.464. Most likely impurity is free carboxylic acid (bromopyruvic or bromoacetic acids). Dissolve in dry Et₂O or dry CHCl₃, stir with CaCO₃ until effecrvescence ceases, filter, (may wash with a little H₂O rapidly), dry (MgSO₄) and distil at least twice. The 2,4-dinitrophenylhydrazone has m 144-145°. [Burros and Holland *J Chem Soc* 672 1947; Letsinger and Laco *J Org Chem* 21 764 1956; Kruse et al. *J Am Chem Soc* 76 5796 1954.] **LACHRYMATORY.**

2-Ethyl-1-butanol [97-95-0] M 102.2, b 146.3°, n¹⁵ 1.4243, n²⁵ 1.4205. Dried with CaSO₄ for several weeks, filtered and fractionally distd.

2-Ethylbut-1-ene [760-21-4] M 84.1, b 66.6°, d 0.833, n 1.423. Washed with saturated aqueous NaOH, then water. Dried with CaCl₂, filtered and fractionally distd.

Ethyl n-butyrate [105-54-4] M 116.2, b 49°/50mm, 119-120°/760mm, d 0.880, n 1.393. Dried with anhydrous CuSO₄ and distd under dry nitrogen.

Ethyl carbamate (urethane) [51-79-6] M 88.1, m 48.0-48.6°. Crystd from *benzene.

Ethyl carbazate (N-ethoxycarbonyl hydrazine) [4114-31-2] M 104.1, m 44-48°, 51-52°, b 95.5°/10m, 92-95°/12mm, 100-102°/11mm. Fractionated using a Vigreux column until the distillate crystallises [Allen and Bell *Org Synth Coll Vol III* 404 1955.]

N-Ethylcarbazole [86-28-2] M 195.3, m 69-70°. Recrystd from EtOH, EtOH/water or isopropanol and dried below 55°.

Ethyl carbonate [105-58-8] M 118.1, b 124-125°, d 0.975, n 1.38287. See diethyl carbonate on p. 203.

Ethyl chloride [75-00-3] M 64.5, b 12.4°, d 0.8978, n 1.3676. Passed through absorption towers containing, successively, conc H₂SO₄, NaOH pellets, P₂O₅ on glass wool, or soda-lime, CaCl₂, P₂O₅. Condensed into a flask containing CaH₂ and fractionally distd. Has also been purified by illumination in the presence of bromine at 0° using a 1000W lamp, followed by washing, drying and distn.

Ethyl chloroacetate [105-39-5] M 122.6, b 143-143.2°, d 1.150, n²⁵ 1.4192. Shaken with satutated aqueous Na₂CO₃ (three times), aqueous 50% CaCl₂ (three times) and saturated aqueous NaCl (twice). Dried with Na₂SO₄ or MgSO₄ and distd. **LACHRYMATORY.**

Ethyl chloroformate [541-41-3] M 108.5, m -81°, b 94-95°, d 1.135, n 1.3974. Washed several times with water, redistd using an efficient fractionating column at atmospheric pressure and a CaCl₂ guard tube to keep free from moisture [Hamilton and Sly *J Am Chem Soc* 47 435 1925; Saunders, Slocombe and Hardy, *J Am Chem Soc* 73 3796 1951]. **LACHRYMATORY AND TOXIC.**

Ethyl chrysanthemate (ethyl \pm 2,2-dimethyl-3{c and t}-[2-methylpropenyl]-cyclopropane carboxylate) [97-41-6] M 196.3, b 98-102°/11mm, 117-121°/20mm. Purified by vacuum distn. The free *trans*-acid has m 54° (from, EtOAc) and the free *cis*-acid has m 113-116° (from EtOAc). The 4-nitrophenyl ester has m 44-45° (from pet ether) [Campbell and Harper *J Chem Soc* 283 1945; IR: Allen et al. *J Org Chem* 22 1291 1957].

Ethyl cinnamate [103-36-6] M 176.2, f 6.7°, b 127°/6mm, 272.7°/768mm, d 1.040, n 1.55983. Washed with aqueous 10% Na₂CO₃, then water, dried (MgSO₄), and distd. The purified ester was saponified with aqueous KOH, and, after acidifying the soln, cinnamic acid was isolated, washed and dried. The ester was reformed by refluxing for 15h the cinnamic acid (25g) with abs EtOH (23g), conc H₂SO₄ (4g) and dry *benzene (100mL), after which it was isolated, washed, dried and distd under reduced pressure [Jeffery and Vogel *J Chem Soc* 658 1958].

Ethyl *trans*-crotonate [623-70-1] M 114.2, b 137°, d 0.917, n 1.425. Washed with aqueous 5% Na₂CO₃, washed with saturated aqueous CaCl₂, dried with CaCl₂ and distd.

Ethyl cyanoacetate [105-56-6] M 113.1, b 206.0°, d 1.061, n 1.41751. Shaken several times with aqueous 10% Na₂CO₃, washed well with water, dried with Na₂SO₄ and fractionally distd.

Ethyl cyanofornate [623-49-4] M 99.1, b 113-114°/740mm, 116.5-116.8°/765.5mm, d₄²⁰ 1.0112, n_D²⁰ 1.3818. Dissolve in Et₂O, dry over Na₂SO₄, filter, evaporate and distil [Malachowsky et al. *Chem Ber* 70 1016 1937; Adickes et al. *J Prakt Chem* [2] 133 313 1932; Grundmann et al. *Justus Liebigs Ann Chem* 577 77 1952].

Ethylcyclohexane [1678-91-7] M 112.2, b 131.8°, d 0.789, n 1.43304, n²⁵ 1.43073. Purified by azeotropic distn with 2-ethoxyethanol, then the alcohol was washed out with water and, after drying, the ethylcyclohexane was redistd.

Ethyl cyclohexanecarboxylate [3289-28-9] M 156.2, b 76-77°/10mm, 92-93°/34mm, d 0.960, n 1.420. Washed with M sodium hydroxide solution, then water, dried with Na₂SO₄ and distd.

Ethyl diazoacetate [623-73-4] M 114.1, m -22°, b 42°/5mm, 45°/12mm, 85-86°/88mm, 140-141°/720mm, 140-143°/atm, d₄^{17.6} 1.0852, n_D^{17.6} 1.4588. A very volatile yellow oil with a strong pungent odour. **EXPLOSIVE [distillation even under reduced pressure is dangerous and may result in an explosion — TAKE ALL THE NECESSARY PRECAUTIONS IF DISTILLATION IS TO BE CARRIED OUT]**. It explodes in contact with conc H₂SO₄ - trace acid causes rapid decomp. It is slightly sol in H₂O, but is miscible with EtOH, *C₆H₆, pet ether and Et₂O. To purify dissolve in Et₂O [using CH₂Cl₂ instead of Et₂O protects the ester from acid], wash with 10% aq Na₂CO₃, dry (MgSO₄), filter and repeat as many times as possible until the Et₂O layer loses its yellow colour, remove the solvent below 20° (vac). Note that prolonged heating may lead to rapid decomp and low yields. It can also be purified by steam distn under reduced pressure but with considerable loss in yield. Place the residual oil in a brown bottle and keep below 10°, and use as soon as possible without distilling. [Womack and Nelson *Org Synth Coll Vol III* 392 1955; UV: Miller and White *J Am Chem Soc* 79 5974 1957; Fieser 1 367 1967.]

Ethyl dibromoacetate [617-33-4] M 245.9, b 81-82°/14.5mm, n²² 1.4973. Washed briefly with conc aqueous NaHCO₃, then with aqueous CaCl₂. Dried with CaSO₄ and distd under reduced pressure.

Ethyl α,β -dibromo- β -phenylpropionate [5464-70-0, *erythro* 30983-70-1] M 336.0, m 75°. Crystd from pet ether (b 60-80°).

Ethyl dichloroacetate [535-15-9] M 157.0, b 131.0-131.5°/401mm, d 1.28, n 1.438. Shaken with aqueous 3% NaHCO₃ to remove free acid, washed with distd water, dried for 3 days with CaSO₄ and distd under reduced pressure.

Ethyl 3,3-diethoxypropionate [10601-80-6] M 190.2, b 58.5°/1.5mm, 65°/2mm, 95-96°/12mm, d_4^{20} 0.78, n_D^{25} 1.4101. Dissolve in dry Et₂O, and dry with solid NaHCO₃, filter and distil and carefully fractionate [Dyer and Johnson *J Am Chem Soc* 56 223 1934].

Ethyl 1,3-dithiane-2-carboxylate [20462-00-4] M 192.3, b 75-77°/0.2mm, 96°/0.4mm, d_4^{20} 1.220, n_D^{25} 1.5379. Dissolve in CHCl₃, wash with aqueous K₂CO₃, 2 x with H₂O, dry over MgSO₄, filter, evaporate and distil. [Eliel and Hartman *J Org Chem* 37 505 1972; Seebach *Synthesis* 1 17 1969.]

Ethyl 1,3-dithiolane-2-carboxylate [20461-99-8] M 178.3, b 85°/0.1mm, d_4^{20} 1.250, n_D^{20} 1.538. Dissolve in CHCl₃, wash with aqueous K₂CO₃, 2 x with H₂O, dry over MgSO₄, filter, evaporate and distil [Hermann et al *Tetrahedron Lett* 2599 1973; Corey and Erickson *J Org Chem* 36 3553 1971].

Ethylene (ethene) [74-85-1] M 28.0, m -169.4°, b -102°/700mm. Purified by passage through a series of towers containing molecular sieves or anhydrous CaSO₄ or a cuprous ammonia soln, then conc H₂SO₄, followed by KOH pellets. Alternatively, ethylene has been condensed in liquid nitrogen, with melting, freezing and pumping to remove air before passage through an activated charcoal trap, followed by a further condensation in liquid air. A sputtered sodium trap has also been used, to remove oxygen.

Ethylene N,N'-bis[(o-hydroxyphenyl)glycine] [1170-02-1] M 360.4, m 249°(dec), $pK_{Est(1)}$ ~1.8, $pK_{Est(2)}$ ~4.8, $pK_{Est(3)}$ ~9.0. Purified by extensive Soxhlet extraction with acetone. [Bonadies and Carrano *J Am Chem Soc* 108 4088 1986].

Ethylene carbonate (1,3-dioxolan-2-one) [96-49-1] M 88.1, m 37°, d 1.32, n^{40} 1.4199. Dried over P₂O₅ then fractionally distd at 10mm pressure. Crystd from dry diethyl ether.

Ethylenediamine (1,2-diaminoethane) [107-15-3] M 60.1, f 11.0°, b 117.0°, d 0.897, n 1.45677, n^{30} 1.4513, pK_1^{25} 6.86, pK_2^{25} 9.92. Forms a constant-boiling (b 118.5°) mixture with water (15%) [hygroscopic and miscible with water]. Recommended purification procedure [Asthana and Mukherjee in J.F.Coetzee (ed), *Purification of Solvents*, Pergamon Press, Oxford, 1982 cf p 53]: to 1L of ethylenediamine was added 70g of type 5A Linde molecular sieves and shaken for 12h. The liquid was decanted and shaken for a further 12h with a mixture of CaO (50g) and KOH (15g). The supernatant was fractionally distd (at 20:1 reflux ratio) in contact with freshly activated molecular sieves. The fraction distilling at 117.2° /760mm was collected. Finally it was fractionally distilled from sodium metal. All distns and storage of ethylenediamine should be carried out under nitrogen to prevent reaction with CO₂ and water. Material containing 30% water was dried with solid NaOH (600g/L), heated on a water bath for 10h. Above 60°, separation into two phases took place. The hot ethylenediamine layer was decanted off, refluxed with 40g of sodium for 2h and distd [Putnam and Kobe *Trans Electrochem Soc* 74 609 1938]. Ethylenediamine is usually distd under nitrogen. Type 5A Linde molecular sieves (70g/L), then a mixture of 50g of CaO and 15g of KOH/L, with further dehydration of the supernatant with molecular sieves has also been used for drying this diamine, followed by distn from molecular sieves and, finally, from sodium metal. A spectroscopically improved material was obtained by shaking with freshly baked alumina (20g/L) before distn.

N,N'-Ethylenediaminediacetic acid (EDDA) [5657-17-0] M 176.2, m 222-224°(dec), pK_1^{25} 6.48, pK_2^{25} 9.57 (for NH groups). Crystd from water.

Ethylenediamine dihydrochloride [333-18-6] M 133.0, pK_1^{25} 6.86, pK_2^{25} 9.92. Crystd from water.

Ethylenediaminetetraacetic acid (EDTA) [60-00-4] M 292.3, m 253°(dec), pK_1^{25} 0.26 pK_2^{25} 0.96, pK_3^{25} 2.60, pK_4^{25} 2.67, pK_5^{25} 6.16, pK_6^{25} 10.26. Dissolved in aqueous KOH or ammonium hydroxide, and pptd with dil HCl or HNO₃, twice. Boiled twice with distd water to remove mineral acid, then recrystd from water or dimethylformamide. Dried at 110°. Also recrystd from boiling 1N HCl, wash crystals with distd H₂O and dried *in vacuo*. [Ma and Ray *Biochemistry* 19 751 1980.]

Ethylene dimethacrylate [97-90-5] M 198.2, b 98-100°/5mm, d 1.053, n 1.456. Distd through a short Vigreux column at about 1mm pressure, in the presence of 3% (w/w) of phenyl-β-naphthylamine.

Ethylene dimyristate [627-84-9] M 482.8, m 61.7°. Crystd from *benzene-MeOH or diethyl ether-MeOH, and dried in a vacuum desiccator.

Ethylene dipalmitate [624-03-3] M 538.9, m 69.1°. Crystd from *benzene-MeOH or diethyl ether-MeOH and dried in a vacuum desiccator.

Ethylene distearate [627-83-8] M 595.0, m 75.3°. Crystd from *benzene-MeOH or diethyl ether-MeOH and dried in a vacuum desiccator.

Ethylene glycol [107-21-1] M 62.1, b 68°/4mm, 197.9°/760mm, d 1.0986, n¹⁵ 1.43312, n²⁵ 1.43056, pK²⁵ 10.6. Very *hygroscopic*, and also likely to contain higher diols. Dried with CaO, CaSO₄, MgSO₄ or NaOH and distd under vacuum. Further dried by reaction with sodium under nitrogen, refluxed for several hours and distd. The distillate was then passed through a column of Linde type 4A molecular sieves and finally distd under nitrogen, from more molecular sieves. Fractionally distd.

Ethylene glycol bis(β-aminoethylether)-N,N'-tetraacetic acid (EGTA) [67-42-5] M 380.4, m >245°(dec), pK₁²⁰ 1.15 (2.40), pK₂²⁰ 2.40 (2.50), pK₃²⁰ 8.40 (8.67), pK₄²⁰ 8.94 (9.22). Dissolved in aq NaOH, pptd by addn of aq HCl, washed with water and dried at 100° *in vacuo*.

Ethylene glycol diacetate [111-55-7] M 146.2, b 190.1°, 79-81°/11mm, d²⁵ 1.4188, n 1.4150. Dried with CaCl₂, filt'd (excluding moisture) fractionally distd under reduced pressure.

Ethylene glycol dibutyl ether [112-48-1] M 174.3, b 78-80°/0.2mm, d 1.105, n 1.42. Shaken with aq 5% Na₂CO₃, dried with MgSO₄ and stored with chromatographic alumina to prevent peroxide formation.

Ethylene glycol diethyl ether (1,2-diethoxyethane) [629-14-1] M 118.2, b 121.5°, d 0.842, n 1.392. After refluxing for 12h, a mixture of the ether (2L), conc HCl (27mL) and water (200mL), with slow passage of nitrogen, the soln was cooled, and KOH pellets were added slowly and with shaking until no more dissolved. The organic layer was decanted, treated with some KOH pellets and again decanted. It was refluxed with, and distd from sodium immediately before use. Alternatively, after removal of peroxides by treatment with activated alumina, the ether has been refluxed in the presence of the blue ketyl formed by sodium-potassium alloy with benzophenone, then distd.

Ethylene glycol dimethyl ether (monoglyme) [110-71-4] M 90.1. See 1,2-dimethoxyethane on p. 210.

Ethylene oxide [75-21-8] M 44.0, b 13.5°/746mm, d¹⁰ 0.882, n⁷ 1.3597. Dried with CaSO₄, then distd from crushed NaOH. Has also been purified by its passage, as a gas, through towers containing solid NaOH.

Ethylene thiourea (2-imidazolidinethione) [96-45-7] M 102.2, m 203-204°. Crystd from EtOH or amyl alcohol.

Ethylene urea (2-imidazolidone) [120-93-4] M 86.1, m 131°. Crystd from MeOH (charcoal).

Ethylenimine (aziridine) [151-56-4] M 43.1, b 55.5°/760mm, d 0.8321, pK²⁵ 8.00. See aziridine on p. 117.

2-Ethylethylenimine [2549-67-9] M 71.1, b 88.5-89°, pK²⁵ 8.31. Freshly distd from sodium before use. **TOXIC**.

Ethyl formate [109-94-4] M 74.1, b 54.2°, d 0.921, d³⁰ 0.909, n 1.35994, n²⁵ 1.3565. Free acid or alcohol is removed by standing with anhydrous K₂CO₃, with occasional shaking, then decanting and

distilling from P_2O_5 . Alternatively, the ester can be stood with CaH_2 for several days, then distd from fresh CaH_2 . Cannot be dried with $CaCl_2$ because it reacts rapidly with the ester to form a crystalline compound.

Ethyl gallate [831-61-8] M 198.2, m 150-151°, 163-165°. Recryst from 1,2-dichloroethane, UV: λ_{max} (neutral species) 275nm (ϵ 10 000); (anion) 235nm (ϵ 10 300), 279nm (ϵ 11 400) and 324nm (ϵ 8 500) [Campbell and Coppinger *J Am Chem Soc* 73 2708 1951].

2-Ethyl-1-hexanol [104-76-7] M 130.2, b 184.3°, d 0.833, n 1.431. Dried with sodium, then fractionally distd.

2-Ethylhexyl vinyl ether [37769-62-3, 103-44-6] M 156.3, b 177-178°/atm. Usually contains amines as polymerization inhibitors. These are removed by fractional distn.

Ethyl hydrocupreine hydrochloride (Optochin) [3413-58-9] M 376.9, m 249-251°, pK_1^{25} 5.50, pK_2^{25} 9.95. Recryst from H_2O [UV: Heidt and Forbes *J Am Chem Soc* 55 2701 1933].

Ethyl iodide (iodoethane) [75-03-6] M 156.0, b 72.4°, d 1.933, n^{15} 1.5682, n^{25} 1.5104. Drying with P_2O_5 is unsatisfactory, and with $CaCl_2$ is incomplete. It is probably best to dry with sodium wire and distil [Hammond et al. *J Am Chem Soc* 82 704 1960]. Exposure of ethyl iodide to light leads to rapid decomposition, with the liberation of iodine. Free iodine can be removed by shaking with several portions of dil aq $Na_2S_2O_3$ (until the colour is discharged), followed by washing with water, drying (with $CaCl_2$, then sodium), and distn. The distd ethyl iodide is stored, over mercury, in a dark bottle away from direct sunlight. Other purification procedures include passage through a 60cm column of silica gel, followed by distn; and treatment with elemental bromine, extraction of free halogen with $Na_2S_2O_3$ soln, followed by washing with water, drying and distn. Free iodine and HI have also been removed by direct distn through a LeBel-Henninger column containing copper turnings. Purification by shaking with alkaline solns, and storage over silver, are reported to be unsatisfactory.

Ethyl isobutyrate [97-62-1] M 116.2, b 110°, d 0.867, n 1.388. Washed with aqueous 5% Na_2CO_3 , then with saturated aqueous $CaCl_2$. Dried with $CaSO_4$ and distd.

Ethyl isocyanate [109-90-0] M 71.1, b 559.8°/759mm, 59-61°/atm, 60-63°/atm, d_4^{20} 0.9031, n_D^{20} 1.3808. Fractionate through an efficient column preferably in an inert atmosphere and store in aliquots in sealed tubes [Bieber *J Am Chem Soc* 74 4700 1952; Slocombe et al. *J Am Chem Soc* 72 1888 1950].

3-Ethylisothionicotinamide [10605-12-6] M 166.2, m 164-166°(dec). Crystd from EtOH.

Ethyl isovalerate [108-64-5] M 130.2, b 134.7°, d 0.8664, n 1.39621, n^{25} 1.3975. Washed with aqueous 5% Na_2CO_3 , then saturated aqueous $CaCl_2$. Dried with $CaSO_4$ and distd.

Ethyl levulinate (4-oxopentanoic acid ethyl ester) [539-88-8] M 144.2, m 37.2°, b 106-108°/2mm, 138.8°/8mm, 203-205°/atm, d_4^{20} 1.012, n_D^{20} 1.423. Stir ester with Na_2CO_3 and charcoal, filter and distil. It is freely soluble in H_2O and EtOH [IR, NMR: Sterk *Monatsh Chem* 99 1770 1968; Thomas and Schuette *J Am Chem Soc* 53 2328 1931; Cox and Dodds *J Am Chem Soc* 55 3392 1933].

Ethyl malonate monoamide [7597-56-0] M 131.1, m 47-50°, 49.5-50°, 50°, b 130-135°/2mm. Crystallise from Et_2O or by slow evaporation of an aqueous soln as colourless crystals [Snyder and Elston *J Am Chem Soc* 76 3039 1954; McAlvain and Schroeder *J Am Chem Soc* 71 45 1949; Rising et al. *J Biol Chem* 89 20 1930].

Ethyl methacrylate [97-63-2] M 114.2, b 59°/100mm, d 0.915, n 1.515. Washed successively with 5% aqueous $NaNO_2$, 5% $NaHSO_3$, 5% $NaOH$, then water. Dried with $MgSO_4$, added 0.2% (w/w) of phenyl- β -naphthylamine, and distd through a short Vigreux column [Schultz *J Am Chem Soc* 80 1854 1958].

Ethyl methyl ether [540-67-0] M 60.1, b 10.8°, d⁰ 0.725. Dried with CaSO₄, passed through an alumina column (to remove peroxides), then fractionally distd.

3-Ethyl-2-methyl-2-pentene [19780-67-7] M 112.2, b 114.5°/760mm. Purified by preparative GLC on a column of 20% squalene on Chromosorb P at 70°.

3-Ethyl-4-methylpyridine [529-21-5] M 121.2, b 76°/12mm, 194.5°/750mm, d 0.947, n 1.510, pK_{Est} ~6.3. Dried with solid NaOH, and fractionally distd.

5-Ethyl-2-methylpyridine [104-90-5] M 121.2, b 178.5°/765mm, d 0.919, n 1.497, pK²⁰ 6.51. Purified by conversion to the picrate, crystn, and regeneration of the free base, then distn.

N-Ethylmorpholine [100-74-3] M 115.2, b 138-139°/763mm, d 0.912, n 1.445, pK²⁵ 7.67. Distd twice, then converted by HCl gas into the hydrochloride (extremely deliquescent) which was crystd from anhydrous EtOH-acetone (1:2) [Herries, Mathias and Rabin *Biochem J* 85 127 1962].

Ethyl nitroacetate [626-35-7] M 133.1, b 42-43°/0.2mm, 71-72°/3mm, 93-96°/9mm, 194-195°/atm, d₄²⁰ 1.1953, n_D²⁰ 1.4260, pK²⁵ 5.82. Purified by repeated distn. IR 1748 (CO₂), 1570 and 1337 (NO₂), and 800cm⁻¹ [Hazeldine *J Chem Soc* 2525 1953]. The *hydrazine salt* crystallises from 95% EtOH or MeOH as yellow crystals m 104-105° [Ungnade and Kissinger *J Org Chem* 22 1661 1957, Emmons and Freeman *J Am Chem Soc* 77 4391 1955].

Ethyl p-nitrobenzoate [99-77-4] M 195.2, m 56°. Dissolved in diethyl ether and washed with aqueous alkali, then the ether was evaporated and the solid recrystd from EtOH.

Ethyl orthoformate [122-51-0] M 148.2, b 144°/760mm, d 0.892, n 1.391. Shaken with aqueous 2% NaOH, dried with solid KOH and distd from sodium through a 20cm Vigreux column.

o-Ethylphenol [90-00-6] M 122.2, f 45.1°, b 210-212°, d 1.020, n 1.537, pK²⁵ 10.20. Purified as for p-ethylphenol below.

p-Ethylphenol [123-07-9] M 122.2, m 47-48°, b 218.0°/762mm, n²⁵ 1.5239, pK²⁵ 10.21. Non-acidic impurities were removed by passing steam through a boiling soln containing 1 mole of the phenol and 1.75 moles of NaOH (as aq 10% soln). The residue was cooled and acidified with 30% (v/v) H₂SO₄, and the free phenol was extracted into diethyl ether. The extract was washed with water, dried with CaSO₄ and the ether was evapd. The phenol was distd at 100mm pressure through a **Stedman** gauze-packed column (see p. 441). It was further purified by fractional crystn by partial freezing, and by zone refining, under nitrogen [Biddiscombe et al. *J Chem Soc* 5764 1963]. Alternative purification is *via* the benzoate, as for phenol.

Ethyl phenylacetate [101-97-3] M 164.2, b 99-99.3°/14mm, d 1.030, n 1.499. Shaken with saturated aqueous Na₂CO₃ (three times), aqueous 50% CaCl₂ (twice) and saturated aqueous NaCl (twice). Dried with CaCl₂ and distd under reduced pressure.

3-Ethyl-5-phenylhydantoin (Ethotoin) [86-35-1] M 204.2, m 94°. Crystd from water.

N-Ethyl-5-phenylisoxazolinium-3'-sulfonate [4156-16-5] M 253.3, m 220°(dec). Crystd from diethyl ether or ethyl acetate/pet ether. [Lamas et al. *J Am Chem Soc* 108 5543 1986.]

3-Ethyl-3-phenyl-2,6-piperidinedione (Glutethimide) [77-21-4] M 217.3, m 84°. Crystd from diethyl ether or ethyl acetate/pet ether.

Ethyl propionate [105-37-3] M 102.1, b 99.1°, d 0.891, n¹⁵ 1.38643, n 1.38394. Treated with anhydrous CuSO₄ and distd under nitrogen.

2-Ethylpyridine [100-71-0] M 107.2, b 148.6°, d 0.942, pK²⁵ 5.89. Dried with BaO, and fractionally distd. Purified by conversion to the picrate, recrystn and regeneration of the free base followed by distn.

4-Ethylpyridine [536-75-4] M 107.2, b 168.2-168.3°, d 0.942, pK²⁵ 6.02. Dried with BaO, and fractionally distd. Also converted to the picrate, recrystd and the free base regenerated and distd.

4-Ethylpyridine-1-oxide [14906-55-9] M 123.1, m 109-110°, pK_{Est}~1.1. Crystd from acetone/ether.

Ethyl pyruvate [617-35-6] M 116.1, m -50°, b 44-45°/10mm, 56°/20mm, 69-71°/42mm, 63°/23mm, 155.5°/760mm, d₄²⁰ 1.047, n_D²⁰ 1.4052. Shake the ester with 10mL portions of satd aq CaCl₂ soln (removes ethyl acetate) and the organic layer is removed by centrifugation, decantation and filtration, and is distilled under reduced pressure. Purification of small quantities is carried out *via* the bisulfite adduct: the ester (2.2mL) is shaken with saturated NaHSO₃ (3.6mL), chill in a freezing mixture when crystals separate rapidly (particularly if seeded). After 5min EtOH (10mL) is added and the crystals are filtered off, washed with EtOH and Et₂O and dried. Yield *ca* 3g of *bisulfite adduct*. Then treat the adduct (16g) with saturated aqueous MgSO₄ (32mL) and 40% formaldehyde (5mL) and shake, whereby the ester separates as an oil which is extracted with Et₂O, the extract is dried (MgSO₄), filtered, evapd and the residue is distd (b 56°/20mm), and then redistd (b 147.5°/750mm) to give 5.5g of pure ester. [Cornforth *Org Synth Coll Vol IV* 467 1963.]

Ethyl Red [2-(4-diethylaminophenylazo)benzoic acid] [76058-33-8] M 197.4, m 150-152°, pK₁ 2.5, pK₂ 9.5. Crystd from EtOH/diethyl ether or toluene. Indicator: pH 4.4 (red) and 6.2 (yellow)

Ethyl stearate [111-61-5] M 312.5, m 33°, b 213-215°/15mm. The solid portion was separated from the partially solid starting material, then crystd twice from EtOH, dried by azeotropic distn with *benzene, and fractionally distd in a spinning-band column at low pressure [Welsh *Trans Faraday Soc* 55 52 1959].

Ethyl thiocyanate (ethyl rhodanide) [542-90-5] M 87.1, b 144-145°, d 1.011, n 1.462. Fractionally distd at atmospheric pressure. (CARE LACHRYMATOR.)

Ethyl thioglycolate [623-51-8] M 120.2, b 50-51°/10mm, 55°/17mm, 62.5-64°/22mm, 67-68°/24mm, 155-158°/atm, d₄²⁰ 1.096, n_D²⁰ 1.457. Dissolve in Et₂O, wash with H₂O, dry over Na₂SO₄, filter, evaporate and distil the residue under reduced pressure [Bredereck et al. *Chem Ber* 90 1837 1957]. The Ni complex [Ni(SCH₂CO₂Et)₂] recrystallised twice from EtOH gives crystals which became black when dried in a vacuum over H₂SO₄, m 104-105° [Dranet and Cefola *J Am Chem Soc* 76 1975 1954].

N-Ethyl thiourea [625-53-6] M 104.2, m 110°. Crystd from EtOH, MeOH or ether.

Ethyl trichloroacetate [515-84-4] M 191.4, b 100-100.5°/30mm, d 1.383. Shaken with saturated aqueous Na₂CO₃ (three times), aqueous 50% CaCl₂ (three times), saturated aqueous NaCl (twice), then distd with CaCl₂ and distd under reduced pressure.

Ethyl trifluoroacetate [383-63-1] M 142.1, b 61.3°/750, 60-62°/atm, 62-64°/755mm, d₄²⁰ 1.191, n_D²⁰ 1.30738. Fractionate through a long Vigreux column. IR has ν at 1800 (CO₂) and 1000 (OCO) cm⁻¹ [Fuson et al. *J Chem Phys* 20 1627 1952; Bergman *J Org Chem* 23 476 1958].

Ethyl trifluoromethanesulfonate [425-75-2] M 178.1, b 115°/atm, 118-120°/atm, d₄²⁰ 1.378, n_D²⁰ 1.336. The ester reacts slowly with H₂O and aqueous alkali. If its IR has no OH bands (~3000 cm⁻¹) then purify by redistillation. If OH bands are present then dilute with dry Et₂O and shake (carefully) with aqueous NaHCO₃ until effervescence ceases, then wash with H₂O and dry (MgSO₄), filter, evaporate and distil the residue under slight vacuum then at atmospheric pressure in a N₂ atmosphere. **IT IS A POWERFUL ALKYLATING AGENT, AND THE FUMES ARE VERY TOXIC - CARRY ALL OPERATIONS IN AN EFFICIENT FUME CUPBOARD.** [Gramstad and Hazeldine *J Chem Soc* 173 1956; Howells and McCown *Chem Rev* 77 69 1977.]

S-Ethyl trifluoroacetate [383-64-2] M 158.1, b 88-90°/atm, 90.5°/760mm, d_4^{20} 1.255, n_D^{20} 1.372. If IR is free of OH bands then fractionate, but if OH bands are present then dilute with dry Et₂O, wash with 5% KOH and H₂O, dry over MgSO₄ and fractionate through an efficient column [Hauptschein et al. *J Am Chem Soc* 74 4005 1952]. *Powerful obnoxious odour.*

Ethyl vinyl ether [109-92-2] M 72.1, b 35.5°, d 0.755. Contains polymerization inhibitors (usually amines, e.g. triethanolamine) which can be removed by fractional distn. Redistd from sodium. **LACHRYMATORY.**

1-Ethynyl-1-cyclohexanol [78-27-3] M 124.2, m 30-33°, 32-33°, b 74°/12mm, 76-78°/17mm, 171-172°/694mm, 180°/atm, d_4^{25} 0.9734, n_D^{25} 1.4801. Dissolve in Et₂O, wash with H₂O, dilute NaHCO₃, H₂O again, dry (Na₂SO₄), filter, evaporate and distil the residue. IR (CCl₄): 3448 (OH), 2941 (CH), 1449-1123 and 956 cm⁻¹; NMR (CCl₄) δ: 3.2 (OH), 2.5 (≡CH), 1.70 (m 10H, CH₂) [Hasbrouck and Kiessling *J Org Chem* 38 2103 1972].

Ethynyl *p*-tolylsulfone [13894-21-8] M 180.2, m 73-74°. Recrystd from pet ether and dried in vac.

Etiocholane (5β-androsterone) [438-23-3] M 260.5, m 78-80°. Crystd from acetone.

Etiocolanic acid [438-08-4] M 304.5, m 228-229°, pK_{Est} ~4.7. Crystd from glacial acetic acid and sublimes at 160°/0.002mm. The *methyl ester* has m 99-101°. [Weiland et al. *Z Physiol Chem* 161 80 1926.]

Etioporphyrin I [448-71-5] M 478.7, m 360-363°. Crystd from pyridine or CHCl₃-pet ether.

Eucaliptol (1,8-cineol, 1,8-epoxy-*p*-menthane, 1,3,3-trimethyl-2-oxabicyclo[2.2.2]-octane) [470-82-6] M 154.2, m 1.3°, 1.5°, b 39-39.3°/4mm, 176-176.4°/760mm, d_4^{20} 0.9232, n_D^{20} 1.4575. Purified by dilution with an equal volume of pet ether, then saturated with dry HBr. The ppt was filtered off, washed with small vols of pet ether, then cineole was regenerated by stirring the crystals with H₂O. It can also be purified *via* its *o*-cresol or resorcinol addition compds. Stored over Na until required. Purified by fractional distn. Insoluble in H₂O but soluble in organic solvents. [IR: Kome et al. *Nippon Kagaku Zasshi [J Chem Soc Japan (Pure Chem Sect)]* 80 66 1959; *Chem Abstr* 603 1961.]

Eugenol (4-allyl-2-methoxyphenol) [97-53-0] M 164.2, b 253°/760mm, 255°/760mm, d_4^{20} 1.066, n_D^{20} 1.540, pK²⁵ 10.19. Fractional distn gives a pale yellow liquid which darkens and thickens on in air. Should store under N₂ at -20°. [Waterman and Priedster *Recl Trav Chim Pays-Bas* 48 1272 1929.]

Eugenol methyl ether (4-allyl-1,2-dimethoxybenzene) [93-15-2] M 178.2, m -4°, b 127-129°/11mm, 146°/30mm, 154.7°/760mm, d_4^{20} 1.0354, n_D^{20} 1.53411. Recrystd from hexane at low temp and redistd (preferably *in vacuo*). [Hillmer and Schorning *Z Phys Chem [A]* 167 407 1934; Briner and Fliszár *Helv Chim Acta* 42 2063 1959.]

(+)-α-Fenchol (1R-1,3,3-trimethyl-norbornan-2-ol) [1632-73-1] M 154.3, m 40-43°, 47-47.5°, b 201-202°, [α]_D²⁰ +12.5° (c 10, EtOH). It is prepared by reduction of (-)-fenchone and is purified by recrystallisation from *C₆H₆-pet ether, or distn, or both. The 2-*carboxybenzoyl* (*monophthalate*) derivative has m 146.5-147.5° [α]_D²⁰ -20.4° (EtOH), and the 2-*phenylurethane* has m 81°. [Beckmann and Metzger *Chem Ber* 89 2738 1956].

(+)-Fenchone (1S-1,3,3-trimethyl-norbornan-2-one) [4695-62-9] M 152.2, m 5-7°, 6.1°, b 63-65°/13mm, 66°/15mm, 122°/10mm, d_4^{20} 0.9434, n_D^{20} 1.4636, [α]_D²⁰ +66.9° (neat, or in c 1.5, EtOH), [α]₅₄₆²⁰ +60.4° (neat). The oily liquid is purified by distn in a vacuum, and is very soluble in EtOH and Et₂O. [Boyle et al. *J Chem Soc, Chem Commun* 395 1971, Hüchel *Justus Liebigs Ann Chem* 549 186 1941; (±)-isomer: Braun and Jacob *Chem Ber* 66 1461 1933.] It forms two *oximes*; *cis-oxime*: m

167° (cryst from pet ether) $[\alpha]_{\text{D}}^{20} +46.5^{\circ}$ (c 2, EtOH), *O*-benzoyloxime **m** 81° $[\alpha]_{\text{D}}^{20} +49^{\circ}$ (EtOH) and *oxime-HCl* **m** 136° (dec). The *trans*-oxime has **m** 123° (cryst from pet ether) $[\alpha]_{\text{D}}^{18} +148^{\circ}$ (c 2, EtOH) and the *O*-benzoyloxime has **m** 125° $[\alpha]_{\text{D}}^{20} +128.5^{\circ}$ (c 2, EtOH) [Hückel *Justus Liebigs Ann Chem* **549** 186 1941; Hückel and Sachs *Justus Liebigs Ann Chem* **498** 166 1932].

(-)- **Fenchone** (1*R*-1,3,3-trimethyl-norbornan-2-one) [7787-20-4] **M** 152.2, **m** 5.2°, **b** 67.2°/10mm, 191-195°/atm, d_4^{20} 0.9484, n_{D}^{20} 1.4630, $[\alpha]_{\text{D}}^{20} -66.8^{\circ}$ (neat). Purification as for the (+)-enantiomer above and should have the same physical properties except for the optical rotations. UV: λ_{max} 285nm (ϵ 12.29). [Braun and Jacob *Chem Ber* **66** 1461 1933; UV: Ohloff et al. *Chem Ber* **90** 106 1957.]

Flavone (2-phenyl-4*H*-1-benzopyran-4-one) [525-82-6] **M** 222.3, **m** 100°. Crystd from pet ether.

Fluoranthene (benzo[*j,k*]fluorene) [206-44-0] **M** 202.3, **m** 110-111°. Purified by chromatography of CCl₄ solns on alumina, with *benzene as eluent. Crystd from EtOH, MeOH or *benzene. Purified by zone melting. [Gorman et al. *J Am Chem Soc* **107** 4404 1985.]

2-Fluorenamine [153-78-6] **M** 181.2. See 2-aminofluorene on p. 106.

9-Fluorenamine [525-03-1] **M** 181.2, **m** 64-65°, $\text{pK}_{\text{Est}} \sim 3.5$. Crystd from hexane.

Fluorene [86-73-7] **M** 166.2, **m** 114.7-115.1°, **b** 160°/15mm. Purified by chromatography of CCl₄ or pet ether (b 40-60°) soln on alumina, with *benzene as eluent. Crystd from 95% EtOH, 90% acetic acid and again from EtOH. Crystn using glacial acetic acid retained an impurity which was removed by partial mercuration and pptn with LiBr [Brown, Dubeck and Goldman *J Am Chem Soc* **84** 1229 1962]. Has also been crystd from hexane, or *benzene/EtOH, distd under vacuum and purified by zone refining. [Gorman et al. *J Am Chem Soc* **107** 4404 1985.]

9-Fluorenone [486-25-9] **M** 180.2, **m** 82.5-83.0°, 85-86°, **b** 341°/760mm. Crystd from absolute EtOH, MeOH or *benzene/pentane. [Ikezawa *J Am Chem Soc* **108** 1589 1986.] Also twice recrystd from toluene and sublimed in a vac [Saltiel *J Am Chem Soc* **108** 2674 1986]. Can be distd under high vacuum.

Fluorene-2,7-diamine [525-64-4] **M** 196.3, **m** 165-166°. Crystd from hot H₂O or aq EtOH, dried in a vac and stored in the dark.

9-Fluorenylmethyl chloroformate (Fmoc-Cl) [28920-43-6] **M** 258.7, **m** 61-63°, 61.4-63°. The IR should contain no OH bands (at ~ 3000 cm⁻¹) due to the hydrolysis product 9-fluorenylmethanol. Purify by recrystn from dry Et₂O. IR (CHCl₃) has band at 1770 cm⁻¹ (C=O) and the NMR (CDCl₃) has δ at 4-4.6 (m 2H, CHCH₂) and 7.1-7.8 (m, 8 aromatic H). The *azide* (Fmoc-N₃) has **m** 89-90° (from hexane) and IR (CHCl₃) at 2135 (N₃) and 1730 (C=O) cm⁻¹; and the *carbazate* (Fmoc-NHNH₂) has **m** 171° dec (from nitromethane), IR (KBr) 3310, 3202 (NH) and 1686 (CONH) cm⁻¹. [Caprino and Han *J Org Chem* **37**, 3404 1972 and *J Am Chem Soc* **92** 5748 1970; Koole et al. *J Org Chem* **59** 1657 1989; Fürst et al. *J Chromatogr* **499** 537 1990.]

9-Fluorenylmethyl succinimidyl carbonate [82911-69-1] **M** 337.3, **m** 147-151° (dec), 151° (dec). Recrystd from CHCl₃-Et₂O, or from pet ether (b 40-60°). [Pauet *Can J Chem* **60** 976 1982; Lapatsaris et al. *Synthesis* 671 1983.]

Fluorescein [9-(*o*-carboxyphenyl-6-hydroxy-3*H*-xanthene-3-one)] [2321-07-5] **M** 320.0, $\epsilon_{495\text{nm}}$ 7.84×10^4 (in 10⁻³M NaOH), pK_1 2.2, pK_2 4.4, pK_3 6.7. Dissolved in dilute aqueous NaOH, filtered and ppted by adding dilute (1:1) HCl. The process was repeated twice more and the fluorescein was dried at 100°. Alternatively, it has been crystd from acetone by allowing the soln to evaporate at 37° in an open beaker. Also recrystd from EtOH and dried in a vacuum oven.

Fluoresceinamine (mixture of 5- and 6-aminofluorescein) [27599-63-9] **M** 347.3, **m** 314-316° (dec, 5-amino) and **m** >200° (dec). Dissolve in EtOH, treat with charcoal, filter, evaporate and dry

residue in vacuum at 100° overnight. Also recrystallise from 6% HCl, then dissolve in 0.5% aqueous NaOH and ppt by acidifying with acetic acid. The separate amines are made from the respective nitro compounds which are best separated *via* their acetate salts. They have similar R_F of 0.26 on Silica Gel Merck F₂₅₄ in 5 mL MeOH + 150 mL Et₂O satd with H₂O. IR (Me₂SO) has a band at 1690 cm⁻¹ (CO₂⁻) and sometimes a weak band at 1750 cm⁻¹ due to lactone. UV (EtOH) of 6-isomer λ_{max} 222 (ϵ 60 000) and 5-isomer λ_{max} 222 (ϵ 60 000) and 285 (ϵ 20.600). [IR: McKinney and Churchill *J Chem Soc (C)* 654 1970; McKinney et al. *J Org Chem* 27 3986 1962; UV: Verbiscar *J Org Chem* 29 490 1964.]

Fluorescein isothiocyanate isomer I (5-isocyanato isomer) [3326-32-7; 27072-45-3 *mixture of 5- and 6-isomers*] **M 389.4, m >160° (slow dec)**. It is made from the pure 5-amino isomer. Purified by dissolving in boiling Me₂CO, filtering and adding pet ether (b 60-70°) until it becomes turbid. If an oil separates then decant and add more pet ether to the supernatant and cool. Orange-yellow crystals separate, collect and dry *in vacuo*. Should give one spot on TLC (silica gel) in EtOAc, pyridine, AcOH (50:1:1) and in Me₂NCHO, CHCl₃, 28% N₄OH (10:5:4). IR (Me₂SO): 2110 (NCS) and 1760 (C=O). The NMR spectra in Me₂CO-d₆ of the 5- and 6-isomers are distinctly different for the protons in the *benzene ring; the UV in phosphate buffer pH 8.0 shows a max at ~490nm. [Sinsheimer et al. *Anal Biochem* 57 227 1974; McKinney et al. *Anal Biochem* 7 74 1964.]

Fluoroacetamide [640-19-7] **M 77.1, m 108°**. Crystd from chloroform.

Fluorobenzene [462-06-6] **M 96.1, b 84.8°, d 1.025, n 1.46573, n³⁰ 1.4610**. Dried for several days with P₂O₅, then fractionally distd.

***o*-Fluorobenzoic acid** [445-29-4] **M 140.1, m 127°, pK²⁵ 3.27**. Crystd from 50% aqueous EtOH, then zone melted or vacuum sublimed at 130-140°.

***m*-Fluorobenzoic acid** [445-38-9] **M 140.1, m 124°, pK²⁵ 3.86**. Crystd from 50% aqueous EtOH, then vacuum sublimed at 130-140°.

***p*-Fluorobenzoic acid** [456-22-4] **M 140.1, m 182°, pK²⁵ 4.15**. Crystd from 50% aqueous EtOH, then zone melted or vacuum sublimed at 130-140°.

3-Fluoro-4-hydroxyphenylacetic acid [458-09-3] **M 170.1, m 33°, pK_{Est(1)}~4.4, pK_{Est(2)}~9.4**. Crystd from water.

1-Fluoro-4-nitrobenzene [350-46-9] **M 141.1, m 27° (stable form), 21.5° (unstable form), b 205.3°/735mm, 95-97.5°/22mm, 86.6°/14mm**. Crystd from EtOH.

1-Fluoro-4-nitronaphthalene [341-92-4] **M 191.2, m 80°**. Recrystd from EtOH as yellow needles [Bunce et al. *J Org Chem* 52 4214 1987].

***o*-Fluorophenol** [367-12-4] **M 112.1, m 16°, b 53°/14mm, d 1.257, n 1.514, pK²⁵ 8.70**. Passed at least twice through a gas chromatographic column for small quantities, or fractionally distd under reduced pressure.

***p*-Fluorophenoxyacetic acid** [405-79-8] **M 170.1, m 106°, pK²⁵ 3.13**. Crystd from EtOH.

4-Fluorophenylacetic acid [405-50-5] **M 154.1, m 86°, pK²⁵ 4.22**. Crystd from heptane.

4-Fluorophenyl isocyanate [1195-45-5] **M 137.1, b 55°/8mm, n_D²⁰ 1.514**. Purify by repeated fractionation through an efficient column. If IR indicated that there is too much urea (in the presence of moisture the symmetrical urea is formed) then dissolve in dry EtOH-free CHCl₃, filter, evaporate and distil. **It is a pungent LACHRYMATORY liquid**. [see Hardy *J Chem Soc* 2011 1934; and Hickinbottom *Reactions of Organic Compounds* Longmans p. 493 1957.]

4-Fluorophenyl isothiocyanate [1544-68-9] M 153.2, m 24-26°, 26-27°, b 66°/2 mm, 215°/atm, 228°/760mm, n_D^{20} 1.6116. Likely impurity is the symmetrical thiourea. Dissolve the isothiocyanate in dry CHCl_3 , filter and distil the residue in a vacuum. It can also be steam distd, the oily layer separated, dried over CaCl_2 and distilled *in vacuo*. *Bis-(4-fluorophenyl)thiourea* has m 145° (from aq EtOH). [Browne and Dyson *J Chem Soc* 3285 1931; Buu Hoi et al. *J Chem Soc* 1573 1955; Olander *Org Synth Coll Vol I* 448 1941].

***p*-Fluorophenyl-*o*-nitrophenyl ether** [448-37-3] M 247.2, m 62°. Crystd from EtOH.

***o*-Fluorotoluene** [95-52-3] M 110.1, b 114.4°, d 1.005, n 1.475. Dried with P_2O_5 or CaSO_4 and fractionally distd through a silvered vacuum-jacketed glass column with 1/8th-in glass helices. A high reflux ratio is necessary because of the closeness of the boiling points of the *o*-, *m*- and *p*- isomers [Potter and Saylor *J Am Chem Soc* 37 90 1915].

***m*-Fluorotoluene** [352-70-5] M 110.1, b 116.5°, d 1.00, n_D^{27} 1.46524. Purification as for *o*-fluorotoluene.

***p*-Fluorotoluene** [352-32-9] M 116.0°, d 1.00, n 1.46884. Purification as for *o*-fluorotoluene.

Formaldehyde [50-00-0] M 30.0, m 92°, b -79.6°/20mm, d_4^{20} 0.815, pK^{25} 13.27 (hydrate). Commonly contains added MeOH. Addition of KOH soln (1 mole KOH: 100 moles HCHO) to 40% formaldehyde soln, or evaporation to dryness, gives paraformaldehyde polymer which, after washing with water, is dried in a vacuum desiccator over P_2O_5 or H_2SO_4 . Formaldehyde is regenerated by heating the paraformaldehyde to 120° under vacuum, or by decomposing it with barium peroxide. The monomer, a gas, is passed through a glass-wool filter cooled to -48° in CaCl_2 /ice mixture to remove particles of polymer, then dried by passage over P_2O_5 and either condensed in a bulb immersed in liquid nitrogen or absorbed in ice-cold conductivity water.

Formaldehyde dimethyl acetal (dimethoxymethane, methylal, formal) [109-87-5] M 76.1, m -108°, b 41-42°/736mm, 41-43°/atm, 42-46°/atm, d_4^{20} 0.8608, n_D^{20} 1.35335. It is a volatile flammable liquid which is soluble in three parts of H_2O , and is readily hydrolysed by acids. Purify by shaking with an equal vol of 20% aq NaOH, stand for 20min, dry over fused CaCl_2 , filter and fractionally distil through an efficient column, store over molecular sieves. [Buchler et al. *Org Synth Coll Vol III* 469 1955; *Ind Eng Chem* 18 1092 1926; Rambaud and Besserre *Bull Soc Chim Fr* 45 1955; IR: *Can J Chem* 36 285 1958.]

Formaldehyde dimethyl mercaptal (bis-[methylthio]methane) [1618-26-4] M 108.2, b 44-47°/13mm, 45.5°/18mm, 148-149°/atm, d_4^{20} 1.0594, n_D^{20} 1.5322. Work in an efficient fume cupboard as the substance may contain traces (or more) of methylmercaptan which has a very bad odour. Dissolve in Et_2O , shake with aqueous alkalis then dry over anhydrous K_2CO_3 , filter and distil over K_2CO_3 under a stream of N_2 . If the odour is very strong then allow all gas effluents to bubble through 5% aqueous NaOH soln which is then treated with dilute KMnO_4 in order to oxidise MeSH to odourless products. UV: λ_{max} 238 nm ($\log \epsilon$ 2.73) [Fehnel and Carmack *J Am Chem Soc* 71 90 1949; Fehér and Vogelbruch *Chem Ber* 91 996 1958; Bøhme and Marz *Chem Ber* 74 1672 1941]. Oxidation with aq KMnO_4 yields *bis-(methylsulfonyl)methane* which has m 142-143° [Fiecchi et al. *Tetrahedron Lett* 1681 1967].

Formamide [75-12-7] M 45.0, f 2.6°, b 103°/9mm, 210.5°/760mm(dec), d 1.13, n 1.44754, n_D^{25} 1.44682. Formamide is easily hydrolysed by acids and bases. It also reacts with peroxides, acid halides, acid anhydrides, esters and (on heating) alcohols; while strong dehydrating agents convert it to a nitrile. It is very *hygroscopic*. Commercial material often contains acids and ammonium formate. Vorhoek [*J Am Chem Soc* 58 2577 1956] added some bromothymol blue to formamide and then neutralised it with NaOH before heating to 80-90° under reduced pressure to distil off ammonia and water. The amide was again neutralised and the process was repeated until the liquid remained neutral on heating. Sodium formate was added, and the formamide was reduced under reduced pressure at 80-90°. The distillate was again neutralised and redistd. It was then fractionally crystd in the absence of CO_2 and water by partial freezing.

Formamide (specific conductance $2 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$) of low water content was dried by passage through a column of 3A molecular sieves, then deionized by treatment with a mixed-bed ion-exchange resin loaded with H^+ and HCONH^- ions (using sodium formamide in formamide) [Notley and Spiro *J Chem Soc (B)* 362 1966].

Formamidine acetate [3473-63-0] **M 104.1, m 159-161°(dec), 164°(dec), $\text{pK}_{\text{Est}} \sim 12$** . Unlike the hydrochloride, the acetate salt is not hygroscopic. It is recrystd from a small volume of acetic acid, by addition of EtOH and the crystals are washed with EtOH then Et₂O and dried in a vac. [Taylor, Ehrhart and Karanisi *Org Synth* 46 39 1966.]

Formamidine sulfinic acid (thiourea-S-dioxide) [1758-73-2] **M 108.1, m 124-126°(dec)**. Dissolved in five parts of aq 1:1% NaHSO₃ at 60-63° (charcoal), then crystd slowly, with agitation, at 10°. Filtered. Dried immediately at 60° [Koniecki and Linch *Anal Chem* 30 1134 1958].

Formanilide [103-70-8] **M 121.1, m 50°, b 166°/14mm, 216°/120mm, d 1.14**. Crystd from ligroin/xylene.

Formic acid [64-18-6] **M 46.0 (anhydr), f 8.3°, b 25°/40mm, 100.7°/760mm, d 1.22, n 1.37140, $n^{25} 1.36938$, $\text{pK}^{25} 3.74$** . Anhydrous formic acid can be obtained by direct fractional distillation under reduced pressure, the receiver being cooled in ice-water. The use of P₂O₅ or CaCl₂ as dehydrating agents is unsatisfactory. Reagent grade 88% formic acid can be satisfactorily dried by refluxing with phthalic anhydride for 6h and then distilling. Alternatively, if it is left in contact with freshly prepared anhydrous CuSO₄ for several days about one half of the water is removed from 88% formic acid: distn removes the remainder. Boric anhydride (prepared by melting boric acid in an oven at a high temperature, cooling in a desiccator, and powdering) is a suitable dehydrating agent for 98% formic acid; after prolonged stirring with the anhydride the formic acid is distd under vacuum. Formic acid can be further purified by fractional crystn using partial freezing.

Forskolin (5-[acetyloxy]-3-ethenyldodecahydro-6,10,10b-trihydroxy-3,4a,7,7,10a-pentamethyl-[3R-{3 α -4 $\alpha\beta$, 5 β , 6 β , 6 $\alpha\alpha$,10 α , 10 $\alpha\beta$, 10 $\beta\alpha$ }-1H-naphtho[2,1-b]pyran-1-one) [66575-29-9] **M 410.5, m 229-232°, 228-233°**. Recrystd from *C₆H₆-pet ether. It is antihypertensive, positive inotropic, platelet aggregation inhibitory and adenylate cyclase activating properties [*Chem Abstr* 89 1978 244150, de Souza et al. *Med Res Rev* 3 201 1983].

D(-)-Fructose [57-48-7] **M 180.2, m 103-106°, $[\alpha]_{546}^{20} -190^\circ$ (after 1h, c 10, H₂O), $\text{pK}^{25} 12.03$** . Dissolved in an equal weight of water (charcoal, previously washed with water to remove any soluble material), filtered and evaporated under reduced pressure at 45-50° to give a syrup containing 90% of fructose. After cooling to 40°, the syrup was seeded and kept at this temperature for 20-30h with occasional stirring. The crystals were removed by centrifugation, washed with a small quantity of water and dried to constant weight under a vacuum over conc H₂SO₄. For higher purity, this material was recrystd from 50% aqueous ethanol [Tsuzuki, Yamazaki and Kagami *J Am Chem Soc* 72 1071 1950].

D(+)-Fucose [3615-37-0] **M 164.2, m 144°, $[\alpha]_{546}^{20} +89^\circ$ (after 24h, c 10 in H₂O)**. Crystd from EtOH.

Fullerene C₆₀ (Buckminsterfullerene C₆₀, Footballene, Buckyball 60) [99685-96-8] **M 720.66 and Fullerene C₇₀** [115383-22-7] **M 840.77**. Purified from the soluble toluene extract (400mg) of the soot (Fullerite) formed from resistive heating of graphite by adsorption on neutral alumina (100g; Brockmann I; 60 x 8cm). Elution with toluene-hexane (5:95 v/v) gives ca 250mg of quite pure C₆₀. It has characteristic spectral properties (see below). Further elution with toluene-hexane (20:80 v/v; i.e. increased polarity of solvent) provides 50mg of "pure" C₇₀ [*J Am Chem Soc* 113 1050 1991].

Chromatography on alumina can be improved by using conditions which favour adsorption rather than crystn. Thus the residue from toluene extraction (1g) in CS₂ (ca 300mL) is adsorbed on alumina (375g, standard grade, neutral ca 150 mesh, Brockmann I) and loaded as a slurry in toluene-hexanes (5:95 v/v) to a 50 x 8cm column of alumina (1.5Kg) in the same solvent. To avoid crystn of the fullerenes, 10% of toluene in hexanes is added quickly followed by 5% of toluene in hexanes after the fullerenes had left the loading fraction (2-3h). With a flow rate of 15mL/min the purple C₆₀ fraction is eluted during a 3-4h period. Evapn of the eluates gives 550-

630mg of product which, after recrystn from CS₂-cyclohexane yields 520-600mg of C₆₀ which contains adsorbed solvent. On drying at 275°/10⁻³mm for 48h a 2% weight loss is observed although the C₆₀ still contains traces of solvent. Further elution of the column with 20% of toluene in hexanes provides 130mg of C₇₀ containing 10-14% of C₆₀ (by ¹³C NMR). This was rechromatographed as above using a half scale column and adsorbing the 130mg in CS₂ (20mL) on alumina (24g) and gave 105mg of recrystd C₇₀ (containing 2% of C₆₀). The purity of C₆₀ can be improved further by washing the crystalline product with Et₂O and Me₂CO followed by recrystn from *C₆H₆ and vacuum drying at high temperatures. [*J Chem Soc, Chem Commun* 956 1992.]

Carbon soot from resistive heating of a carbon rod in a partial helium atmosphere (0.3bar) under specified conditions is extracted with boiling *C₆H₆ or toluene, filtered and the red-brown soln evapd to give crystalline material in 14% yield which is mainly a mixture of fullerenes C₆₀ and C₇₀. Chromatographic filtration of the 'crude' mixture with *C₆H₆ allows no separation of components, but some separation was observed on silica gel TLC with *n*-hexane or *n*-pentane, but not cyclohexane. Analytical HPLC with hexanes (5µm Econosphere silica) gave satisfactory separation of C₆₀ and C₇₀ (retention times of 6.64 and 6.93min respectively) at a flow rate of 0.5mL/min and using a detector at 256nm. HPLC indicated the presence of minor (<1.5% of total mass) unidentified C_n with species (retention times of 5.86 and 8.31min. Column chromatography on flash silica gel with hexanes gives a few fractions of C₆₀ with ≥95% purity but later fractions contain mixtures of C₆₀ and C₇₀. These can be obtained in 99.85 and >99% purity respectively by column chromatography on neutral alumina. [*J Phys Chem* 94 8630 1990].

Separation of C₆₀ and C₇₀ can be achieved by HPLC on a dinitroanilinopropyl (DNAP) silica (5µm pore size, 300Å pore diameter) column with a gradient from *n*-hexane to 50% CH₂Cl₂ using a diode array detector at wavelengths 330nm (for C₆₀) and 384nm (for C₇₀). [*J Am Chem Soc* 113, 2940, 1991.]

Soxhlet extraction of the "soot" is a good preliminary procedure, or if material of only *ca* 98% purity is required. Soxhlet extraction with toluene is run (20min per cycle) until colourless solvent filled the upper part of the Soxhlet equipment (10h). One third of the toluene remained in the pot. After cooling, the solution was filtered through a glass frit. This solid (purple in toluene) was *ca* 98% C₆₀. This powder was again extracted in a Soxhlet using identical conditions as before and the C₆₀ was recrystd from toluene to give 99.5% pure C₆₀. C₇₀ has greater affinity than C_{h60} for toluene. [*J Chem Soc, Chem Commun* 1402 1992.]

Purification of C₆₀ from a C₆₀/C₇₀ mixture was achieved by dissolving in an aqueous soln of γ (but not β) cyclodextrin (0.02M) upon refluxing. The rate of dissolution (as can be followed by UV spectra) is quite slow and constant up to 10⁻⁵M of C₆₀. The highest concn of C₆₀ in H₂O obtained was 8 x 10⁻⁵M and a 2 γ-cyclodextrin:1 C₆₀ clathrate is obtained. C₆₀ is extracted from this aqueous soln by toluene and C₆₀ of >99 purity is obtained by evaporation. With excess of γ-cyclodextrin more C₆₀ dissolves and the complex precipitates. The ppte is insol in cold H₂O but sol in boiling H₂O to give a yellow soln. [*J Chem Soc, Chem Commun* 604 1922.]

C₆₀ and C₇₀ can also be readily purified by inclusion complexes with *p*-*tert*-butylcalix[6] and [8]arenes. Fresh carbon-arc soot (7.5g) is stirred with toluene (250mL) for 1h and filtered. To the filtrate is added *p*-*tert*-butylcalix[8]arene, refluxed for 10min and filtered. The filtrate is seeded and set aside overnight at 20°. The C₆₀ complex separated as yellow-brown plates and recrystd twice from toluene (1g from 80mL), 90% yield. Addition of CHCl₃ (5mL) to the complex (0.85g) gave C₆₀ (0.28g, 92% from recryst complex).

p-*tert*-Butylcalix[6]arene-(C₆₀)₂ complex is prepared by adding to a refluxing soln of C₆₀ (5mg) in toluene (5mL), *p*-*tert*-butylcalix[6]arene (4.4mg). The hot soln was filtered rapidly and cooled overnight to give prisms (5.5mg, 77% yield). Pure C₆₀ is obtained by decomposing the complex with CHCl₃ as above.

The *p*-*tert*-butylcalix[6]arene-(C₇₀)₂ complex is obtained by adding *p*-*tert*-butylcalix[6]arene (5.8mg) to a refluxing soln of C₇₀ (5mg) in toluene (2mL), filtering hot and slowly cooling. to give red-brown needles (2.5mg, 31% yield) of the complex. Pure C₇₀ is then obtained by decomposing the complex with CHCl₃.

Decomposition of these complexes can also be achieved by boiling a toluene soln over KOH pellets for *ca* 10min. The calixarenes form Na salts which do not complex with the fullerenes. These appear to be the most satisfactory means at present for preparing large quantities of relatively pure fullerene C₆₀ and C₇₀ and is considerably cheaper than previous methods. [*Nature* 368 229 1994.]

Repeated chromatography on neutral alumina yields minor quantities of solid samples of C₇₆, C₈₄, C₉₀ and C₉₄ believed to be higher fullerenes. A stable oxide C₇₀O has been identified. Chromatographic procedures for the separation of these compounds are reported. [*Science* 252 548 1991.]

Physical properties of Fullerene C₆₀: It does not melt below 360°, and starts to sublime at 300° *in vacuo*. It is a mustard coloured solid that appears brown or black with increasing film thickness. It is soluble in common organic solvents, particularly aromatic hydrocarbons which give a beautiful magenta colour. Toluene solutions are purple in colour. Sol in *C₆H₆ (5mg/mL), but dissolves slowly. Crysts of C₆₀ are both needles and plates. UV-Vis in hexanes: λ_{max} nm(log ε) 211(5.17), 227sh(4.91), 256(5.24), 328(4.71), 357sh(4.08), 368sh(3.91), 376sh(3.75), 390(3.52), 395sh(3.30), 403(3.48), 407(3.78), 492sh(2.72) < 540(2.85), 568(2.78), 590(2.86), 598(2.87) and 620(2.60). IR (KBr): ν 1429m, 1182m, 724m, 576m and 527s cm⁻¹. ¹³C NMR: one signal at 142.68ppm.

Physical properties of Fullerene C₇₀: It does not melt below 360°, and starts to sublime at 350° *in vacuo*. A reddish-brown solid, greenish black in thicker films. Solns are port-wine red in colour. Mixtures of C₆₀ and C₇₀ are red due to C₇₀ being more intensely coloured. It is less soluble than C₆₀ in *C₆H₆ but also dissolves slowly. C₇₀ gives orange coloured soln in toluene. Drying at 200-250° is not sufficient to remove All solvent. Samples need to be sublimed to be free from solvent.

UV-Vis in hexanes: λ_{max} nm(log ε) 214(5.05), 235(5.06), 249sh(4.95), 268sh(4.78), 313(4.23), 330(4.38), 359(4.29), 377(4.45), 468(4.16), 542(3.78), 590sh(3.47), 599sh(3.38), 609(3.32), 623sh(3.09), 635sh(3.13) and 646sh(2.80).

IR (KBr): ν 1430m, 1428m, 1420m, 1413m, 1133mw, 1087w, 795s, 674ms, 642ms, 5778s, 566m, 535ms and 458m cm⁻¹.

¹³C NMR [run in the presence of Cr(pentan-2,4-dione)₃ which induces a *ca* 0.12ppm in the spectrum]: Five signals at 150.07, 147.52, 146.82, 144.77 and 130.28ppm, unaffected by proton decoupling.

[Further reading: Kroto, Fischer and Cox *Fullerenes* Pergamon Press, Oxford 1993 ISBN 0080421520; Kadish and Ruoff (Eds) *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials* The Electrochemical Soc. Inc, Pennington, NJ, 1994 ISBN 1566770823]

Fumagillin {2,4,6,8-decatetraene-1,10-dioic acid mono[4-(1,2-epoxy-1,5-dimethyl-4-hexenyl)-5-methoxy-1-oxaspiro[2.5]oct-6-yl] ester} [23110-15-8] M 458.5, m 194-195°, [α]_D²⁰ -26.2° (in 95% EtOH), pK_{Est} ~4.5. Forty grams of a commercial sample containing 42% fumagillin, 45% sucrose, 10% antifoam agent and 3% of other impurities were digested with 150mL of CHCl₃. The insoluble sucrose was filtered off and washed with CHCl₃. The combined CHCl₃ extracts were evap almost to dryness at room temperature under reduced pressure. The residue was triturated with 20mL of MeOH and the fumagillin was filtered off by suction. It was crystd twice from 500mL of hot MeOH by standing overnight in a refrigerator (yellow needles). (The long chain fatty ester used as antifoam agent was still present, but was then removed by repeated digestion, on a steam bath, with 100mL of diethyl ether.) For further purification, the fumagillin (10g) was dissolved in 150mL of 0.2M ammonia, and the insoluble residue was filtered off. The ammonia soln (cooled in running cold water) was then brought to pH 4 by careful addn of M HCl with constant shaking in the presence of 150mL of CHCl₃. (Fumagillin is acid-labile and must be removed rapidly from the aq acid soln.) The CHCl₃ extract was washed several times with distd water, dried (Na₂SO₄) and evaporated under reduced pressure. The solid residue was washed with 20mL of MeOH. The fumagillin was filtered by suction, then crystd from 200mL of hot MeOH. [Tarbell et al. *J Am Chem Soc* 77 5610 1955.]

Alternatively, 10g of fumagillin in 100mL CHCl₃ was passed through a silica gel (5g) column to remove tarry material, and the CHCl₃ was evaporated to leave an oil which gave fumagillin on crystn from amyl acetate. It recrystallises from MeOH (charcoal). The fumagillin was stored in dark bottles in the absence of oxygen and at low temperatures. [Schenk, Hargie and Isarasena *J Am Chem Soc* 77 5606 1955.]

Fumaraldehyde bis-(dimethyl acetal) (trans-1,1,4,4-tetramethoxybut-2-ene) [6068-62-8] M 176.2, b 100-103°/15mm, 101-103°/25mm, d₄²⁰ 1.011, n_D²⁰ 1.425. Dry over fused CaCl₂ and dist *in vacuo*. The maleic (cis) isomer has b 112°/11mm, and d₄²³ 0.932 and n_D²⁵ 1.4243. [Zeik and Heusner *Chem Ber* 90 1869 1957; Clauson-Kaas et al. *Acta Chem Scand* 9 111 1955; Clauson-Kaas *Acta Chem Scand* 6 569 1952.]

Fumaric (trans-but-2-ene-1,4-dioic) acid [110-17-8] M 116.1, m 289.5-291.5° (sealed tube), pK₁²⁵ 3.10, pK₂²⁵ 4.60 (4.38). Crystd from hot M HCl or water. Dried at 100°.

Furan [110-00-9] M 68.1, b 31.3°, d 1.42, n 1.4214. Shaken with aqueous 5% KOH, dried with CaSO₄ or Na₂SO₄, then distd under nitrogen, from KOH or sodium, immediately before use. A trace of hydroquinone could be added as an inhibitor of oxidation.

3-(2-Furanyl)acrylic acid [539-47-9] M 138.1, m 141°, pK_{Est} ~3.8. Crystd from H₂O or pet ether (b 80-100°)(charcoal).

Furan-2-carboxylic (2-furoic) acid [88-14-2] M 112.1, m 133-134°, b 141-144°/20mm, 230-232°/760mm, pK₁²⁵ -7.3 (O-protonation), pK₂²⁵ 3.32. Crystd from hot water (charcoal), dried at 120° for 2h, then recrystd from CHCl₃, and again dried at 120° for 2h. For use as a standard in volumetric analysis, good quality commercial acid should be crystd from CHCl₃ and dried as above or sublimed at 130-140° at 50-60mm or less.

Furan-3-carboxylic (3-furoic) acid [488-93-7] M 112.1, m 122-123°, pK²⁵ 4.03 Crystd from water.

Furan-3,4-dicarboxylic acid [3387-26-6] M 156.1, m 217-218° pK₁²⁵ 1.44, pK₂²⁵ 7.84. Crystd from water.

Furfural (2-furfuraldehyde) [98-01-1] M 96.1, b 54-56°/11mm, 59-60°/15mm, 67.8°/20mm, 90°/65mm, 161°/760mm, d₄²⁰ 1.159, n_D²⁰ 1.52608, pK -6.5 (O-protonation). Unstable to air, light and acids. Impurities include formic acid, β-formylacrylic acid and furan-2-carboxylic acid. Distd over an oil bath from 7% (w/w) Na₂CO₃ (added to neutralise acids, especially pyromucic acid). Redistd from 2% (w/w) Na₂CO₃, and then, finally fractionally distd under vacuum. It is stored in the dark. [Evans and Aylesworth *Ind Eng Chem (Anal ed)* 18 24 1926.]

Impurities resulting from storage can be removed by passage through chromatographic grade alumina. Furfural can be separated from impurities other than carbonyl compounds by the bisulfite addition compound. The aldehyde is steam volatile.

It has been purified by distn (using a Claisen head) under reduced pressure. This is essential as is the use of an oil bath with temperatures of no more than 130° are highly recommended. When furfural is distd at atm press (in a stream of N₂), or under reduced pressure with a free flame (caution because the aldehyde is flammable) an almost colourless oil is obtained. After a few days and sometimes a few hours the oil gradually darkens and finally becomes black. This change is accelerated by light but occurs more slowly when kept in a brown bottle. However, when the aldehyde is distd under vacuum and the bath temperature kept below 130° during the distn, the oil develops only a slight colour when exposed to direct sunlight during several days. The distn of very impure material should NOT be attempted at atm pressure otherwise the product darkens rapidly. After one distn under vacuum a distn at atmospheric pressure can be carried out without too much decomposition and darkening. The liquid **irritates mucous membranes**. Store in dark containers under N₂. [Adams and Voorhees *Org Synth Coll Vol I* 280 1941.]

Furfuryl alcohol (2-furylmethanol) [98-00-0] M 98.1, b 68-69°/20mm, 170.0°/750mm, d 1.132, n 1.4873, n³⁰ 1.4801, pK²⁵ 2.61. Distd under reduced pressure to remove tarry material, shaken with aqueous NaHCO₃, dried with Na₂SO₄ and fractionally distd under reduced pressure from Na₂CO₃. Further dried by shaking with Linde 5A molecular sieves.

Furfurylamine (2-aminomethylfuran) [617-89-0] M 97.1, b 142.5-143°/735mm, d 1.059, n 1.489, pK³⁰ 8.89. Distd under nitrogen from KOH through a column packed with glass helices.

Furil [492-94-4] M 190.2, m 165-166°. Crystd from MeOH or *benzene (charcoal).

Furoin [552-86-3] M 192.2, m 135-136°. Crystd from MeOH (charcoal).