EXPERIMENTAL[4]

A mixture of 120 g. of vinyl phenyl ether,[5,6] 150 g. of acetic acid, and 150 g. of dimethylaniline was refluxed for 2.5 hours under nitrogen. The reaction mixture was decomposed with cold dilute hydrochloric acid, extracted with ether, and distilled at 20 mm. through a 23-plate Fenske-type column to give 152 g. of 1-phenoxyethyl acetate (85% yield) plus 4 g. of recovered vinyl phenyl ether. The following constants were obtained on a heart cut of the material: b.p. 119°/20 mm., n_D^{25} 1.4870, d_4^{25} 1.0715, t_f −10.76° ± 0.01[7] (calc'd mole-% purity, 99.2–99.6).

Anal. Calc'd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; Mol. wt., 180. Found: C, 66.44; H, 6.74; Mol. wt., 182.

Alkaline hydrolysis was accomplished by boiling 9 g. of 1-phenoxyethyl acetate for 1 hour with 45 cc. of 10% aqueous potassium hydroxide under a 50-cm. Vigreux column. Acidification of the pot residue gave 4.1 g. (87% yield) of crude phenol, identified as phenoxyacetic acid; m.p. and mixture m.p. 97–98°. The aqueous distillate contained acetaldehyde, identified as its dimedon derivative; m.p. and mixture m.p. 139–141°. [Attempts to determine the saponification equivalent of 1-phenoxyethyl acetate by standard procedure (refluxing for 2 hours with an excess of 0.7 *N* base, followed by back-titration) gave the low value of 165 instead of the theoretical 180].

Acid hydrolysis was accomplished by refluxing 1 g. of 1-phenoxyethyl acetate for 2 hours with a mixture of 2 g. of 2,4-dinitrophenylhydrazine, 15 cc. of concentrated sulfuric acid, and 150 cc. of 95% ethanol. One gram of crude acetaldehyde dinitrophenylhydrazone (81% yield) was obtained: m.p. and mixture m.p. of once-crystallized material 166–168°.

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(4) All melting and boiling points are uncorrected; t_f is corrected.

(5) Insinger, U. S. Patent 2,615,050 (1952); Brit. Patent 656,556 (1951); *Chem. Abstr.*, **46**, 8149 (1952).

(6) Shostakovskii and Burmistrova, *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik*, **2**, 48 (1950); *Chem. Abstr.*, **48**, 627 (1954).

(7) t_f = freezing temperature determined by extrapolation of freezing curve; temperature measured by platinum resistance thermometer and G-2 Mueller bridge which had been certified by the National Bureau of Standards.

Marine Sterols. II. 24-Methylenecholesterol in Molluscs

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A new sterol, 24-methylenecholesterol, has recently been isolated from two species of the class pelecypoda, oyster, *Ostrea virginica* and clam, *Saxidomus giganteus*.[1] From the viewpoint of the comparative biochemistry of sterols it was of interest to further investigate the occurrence of 24-methylenecholesterol in pelecypoda.

This paper reports the occurrence of 24-methylenecholesterol in three other members of the same class, scallop, *Pecten caurinus*, cockle, *Cardium corbis*, and in a commercially prepared crude sterol mixture from mussel *Modiolus demissus*.[2]

The chromatographic pattern of *p*-phenylazobenzoyl (azoyl) esters of scallop, cockle, and mussel sterols resembled that of oyster and clam. The minor top zone ($\Delta^{5,7}$-sterol) was absent, zone 1 consisted of 24-methylenecholesterol, zone 2 of a diunsaturated, and zone 3 of a monounsaturated sterol.

The identity of these bands with the corresponding bands in the chromatogram of oyster and clam sterol azoyl esters was indicated by a comparison of the infrared spectra of the free sterols.

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EXPERIMENTAL[3]

Preparation of crude sterols. Commercially packed frozen scallop muscle (6.58 kg.) was ground up with an equal weight of sodium sulfate and the mixture was shaken with two 15 l. portions of petroleum ether (b.p. 65–110°). By evaporation of the solvent 8.0 g. of fat were obtained. Further shaking with the same volume of chloroform yielded 32.8 g. (total fat 0.62%). The fat was saponified for 2 hours in 10% ethanolic potassium hydroxide and the non-saponifiable matter, 9.4 g. (23.0%) of yellow solid, was dissolved in methanol. Cooling precipitated 6.49 g. (69.0%) of sterols melting at 130–132°, recrystallized m.p. 132–133° $[\alpha]_D^{22}$ −37.7°. The addition of water to the non-saponifiables supernatant precipitated 390 mg. of sterols, m.p. 124–126°.

In the case of cockle the entire contents of the shell (278 g.) were extracted with three 1000-ml. portions of acetone; when the solvent was evaporated and the remaining water suspension was extracted with ether, 7.5 g. (2.7%) of fat were obtained. Phosphatides were precipitated by the addition of magnesium chloride to an acetone solution of the fat. Saponification for 2 hours in 10% ethanolic potassium hydroxide yielded 950 mg. (12.7%) of non-saponifiable matter. Recrystallization from methanol gave 390 mg. (41.1%) of sterols m.p. 129–131°, $[\alpha]_D^{22}$ −30.6°.

Mussel sterols were obtained by recrystallization of the commercially prepared, crude sterol mixture.[2]

Chromatography. p-Phenyl azobenzoyl esters of scallop, cockle and mussel sterols were chromatographed on silicic acid-Celite employing the same technique as in the case of oyster and clam.[1,4]

Scallop esters separated into three closely running bands of approximately equal intensity. There was 34.6% of 24-methylenecholesterol. Because of the relatively low concentration of zone 2 (16.7%), cockle sterols appeared to separate into only two nearly equally intense bands, but after the chromatogram had been extruded a faint band appeared be-

(1) Idler and Fagerlund, *J. Am. Chem. Soc.*, **77**, 4142 (1955).

(2) Bergmann and Ottke, *J. Org. Chem.*, **14**, 1085 (1949).

(3) Melting points are uncorrected. Optical rotations were measured by means of a Rudolph precision polarimeter. Infrared spectra were recorded of solid films with a Perkin-Elmer doublebeam infrared spectrophotometer.

(4) Idler and Baumann, *J. Biol. Chem.*, **195**, 623 (1952).

tween the two major components. 24-Methylenecholesterol represented 53.3% of the sterols of cockle. The distribution of the zones of scallop and mussel together with that of oyster and clam is shown in Table I.

TABLE I

DISTRIBUTION OF AZOYL ESTERS IN PELECYPODA

	Oyster, %	Clam, %		Scallop, %	Cockle, %
Zone 1	5.0	3.0			
Zone 2	36.1	53.0	Zone 1	34.6	53.3
Zone 3	28.6	21.3	Zone 2	39.4	16.7
Zone 4	30.3	22.7	Zone 3	26.0	30.0

Mussel azoyl esters also separated into three zones on the column. 24-Methylenecholesterol represented 5.4% of the total azoyl esters. Since, however, the commercial sterol mixture had previously undergone crystallization for removal of 7-dehydrosterols[2] no conclusions could be drawn about the original composition of mussel sterols.

Properties of 24-methylenecholesterol and derivatives. Zone 1 azoyl ester from scallop crystallized from benzene-aq. ethanol, m.p. 197°; mixed with azoyl ester of 24-methylenecholesterol from oyster,[1] m.p. 196°. The azoyl ester was hydrolyzed[5] and the acetate was prepared. Ultraviolet absorption and the modified Liebermann-Burchard reaction[6,7] of the crude acetate showed the presence of 2.6% of $\Delta^{5,7}$ sterols (calc'd as ergosterol) which were removed with maleic anhydride in the usual manner.[1] The recrystallized acetate of zone 1 melted at 136°, mixture m.p. 136° with 24-methylenecholesterol, $[\alpha]^{22}_{D}$ −42.9°.

Anal. Calc'd for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98. Found: C, 81.71; H, 10.88.

The *acetate* was hydrolyzed and the *sterol* was crystallized from methanol, m.p. 141°, mixture m.p. 141° with 24-methylenecholesterol, $[\alpha]^{22}_{D}$ −35.7°.

The *benzoate* melted at 147°, undepressed on admixture with 24-methylenecholesterol benzoate, $[\alpha]^{22}_{D}$ −14.2°.

24-Ketocholesteryl acetate and derivatives. The acetate of zone 1 in cold glacial acetic acid-acetic anhydride (1:1) was treated with 2 equivalents of ozone. The ozonolysis product was worked up as previously described.[1] Subsequent crystallization from methanol yielded a substance with the m.p. 127°, $[\alpha]^{22}_{D}$ −43.1°. Mixture m.p. with 24-ketocholesterol from oyster and a synthetic product was 127°. *24-Ketocholesterol acetate oxime* was prepared by refluxing with hydroxylamine hydrochloride in pyridine-ethanol. Two recrystallizations from aq. ethanol gave m.p. 169°, mixture m.p. 169° with the synthetic material.

Anal. Calc'd for $C_{29}H_{47}NO_3$: C, 76.10; H, 10.35; N, 3.06. Found: C, 76.34; H, 10.56; N, 2.94.

24-Ketocholesterol acetate 2,4-dinitrophenylhydrazone was recrystallized from ethanol. M.p. 169°, mixture m.p. 169° with the synthetic product.

Anal. Calc'd for $C_{35}H_{50}N_4O_6$: C, 67.50; H, 8.09. Found: C, 67.38; H, 8.22.

24-Methylenecholesterol from cockle and mussel. 24-Methylenecholesterol and derivatives were prepared from zone 1 of cockle and mussel identically as described above for scallop. The preparations contained only insignificant quantities of Δ^7-sterols. The properties of the sterol and of the azoyl ester, acetate, and benzoate were identical with those of 24-methylenecholesterol from oyster, clam, and scallop.

Infrared spectra. The identify of 24-methylenecholesterol from the five sources so far investigated was confirmed by a comparison in detail of their infrared spectra. The spectrum of 24-methylenecholesterol showed the maxima at 890 and 1640 cm^{-1} characteristic of the methylene group.[1] Other changes in the spectrum caused by introduction of the 24 (28) double bond were a sharp (weak) peak at 3050 cm^{-1} and a broader (weak) band at 1750–1790 cm^{-1}. These data were derived from a comparison of the spectrum of 24-methylenecholesterol with those of its neutral reduction product (Adams' catalyst in ethyl acetate) and of campesterol.

The infrared spectra of zone 2 from scallop, cockle, and mussel and the diunsaturated zone 3 from oyster and clam were compared and found to be identical. The second double bond does not introduce any major bands. A comparison with the spectra of Δ^5-sterols showed the following characteristics: Absence of the weak band at 925 cm^{-1}; a dominant shoulder at 965–975 cm^{-1}; absence of the weak peak at 1240 cm^{-1}; shifting of the weak band at 1305 cm^{-1} to 1295 cm^{-1}; absence of the shoulder at 1360 cm^{-1}. The monounsaturated bottom zone from oyster, clam, scallop, cockel, and mussel produced a spectrum typical of Δ^5-sterols. The clam and scallop sterol has been reduced to a stanol with Adams' catalyst in glacial acetic acid but the product and its derivatives do not possess the properties of any previously described unsaturated sterol.

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(5) Idler, Nicksic, Johnson, Meloche, Schuette, and Baumann, *J. Am. Chem. Soc.*, **75**, 1712 (1953).

(6) Idler and Baumann, *J. Biol. Chem.*, **195**, 615 (1952).

(7) Idler and Baumann, *J. Biol. Chem.*, **203**, 389 (1953).

The Addition of Azide Ion to Epoxides[1]

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From the original rate correlation of Swain and Scott[2] in conjunction with work performed at the Jet Propulsion Laboratory on the kinetics of the addition of nitrate ion to the ethylene oxide ring,[3] it was observed that the rate of addition of the azide ion to epoxides is relatively high in comparison with that of other nucleophilic species. Therefore, azidoalcohols may be prepared readily in aqueous solution, under mild conditions by nucleophilic attack of epoxides by azide ions. In a recent publication,[4] the reaction of sodium azide with representative epoxides has been aptly studied, and the structure proof of the resulting azidoalcohols has been presented. The present note contains improved synthetic procedures for the preparation of azidoalcohols by this reaction. In addition, some new compounds, including glycidyl azide, have been prepared.

The relatively harsh conditions employed by

(1) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495-Ord 18, sponsored by the Department of the Army, Ordnance Corps.

(2) Swain and Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

(3) Petty and Nichols, *J. Am. Chem. Soc.*, **76**, 4385 (1954).