

gave three spots indicating mono-saccharides (Fig. 3A and its legend) and five spots indicating amino acids (Fig. 3B). After careful testing, the spot No. 1 of Figs. 3A and 3B was identified as neuramic acid in its keto or pyranose form.

The cetylpyridinium chloride precipitated *Paracentrotus* jelly which was subjected to hydrolysis contained as dominating component fucose but also in minor quantity glucose. Moreover neuramic acid is present as an important component, see Figs. 3 and 4. In natural or precipitated but not hydrolyzed jelly this last component is present in the form of *N*-acetylneuramic acid. Figs. 3B and 4 show furthermore the presence in the hydrolysate of four amino acids (alanine, aspartic acid, glutamic acid, glycine). In addition, the hydrolysate contains sulfate and calcium.

The presence of neuramic acid was detected also in the jelly substance precipitated with cetylpyridinium chloride or ethanol of *Arbacia* and *Sphaerechinus*. It was also found as component in acid mucopolysaccharides which were isolated from eggs and embryos of the three sea urchin species studied.

Discussion. The results reported above raise the question as to whether *N*-acetylneuramic acid constitutes an integrated part of the jelly coat substance or whether its presence is of a more fortuitous nature caused by its diffusion from the egg surface. A dual origin of components of the jelly coat is made probable through the immunological studies carried out by Baxandall, Perlmann and Afzelius^{8,10} and by Baxandall.¹¹ Moreover the question arises as to whether the presence of *N*-acetylneuramic acid contributes to the species specific agglutination of spermatozoon exhibited in many species by the jelly coat substance. These questions are subject to further work.

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Pyrimidines from Malonyl Chloride and Nitriles

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In 1962 Davis, Elvidge and Foster¹ described a reaction between malonyl chloride and α -methylene nitriles leading to 3-substituted 2-chloro-4,6-dihydropyridines, considered to exist in the α -pyridone form. Attempted extension of this reaction to α -halogenonitriles unexpectedly afforded 2-substituted 4-chloro-6-pyrimidones.^{2,3} Thus fluoroacetonitrile gave (I), substantiated by UV, IR, NMR, and mass spectra, and by hydrogenolysis to the known 2-methyl-4-pyrimidone (II).⁴ As reported,² bromoacetonitrile and α -bromopropionitrile likewise gave (III) and (IV), respectively, but chloroacetonitrile gave a mixture of pyridine (IX) and pyrimidine (V) products. Reinvestigation of the earlier work confirmed the claims¹ with one exception:^{2,3} this was that acetonitrile yielded the pyrimidone (VI) and not a pyridine as had been thought from the m.p. and Cl analysis. Part of the new identification of (VI) involved hydrogenolysis to (II). In amplification of the reaction between propionitrile and malonyl chloride,¹ it was observed^{2,3} that the main, pyridine product (X) was accompanied by traces of the pyrimidine (VII).

Meanwhile, Bernatek and Stensrud encountered the malonyl chloride-nitrile reaction during some other work and found⁵ that the product (m.p. 233°) from acetonitrile must be a pyrimidine (VI).

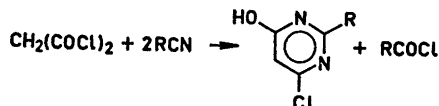
(Found: C 41.3; H 3.4; N 19.7; Cl 24.4. Calc. for $C_5H_5N_2OCl$: C 41.5; H 3.5; N 19.4; Cl 24.5). Methyl (3 protons) at $\tau=7.68$. A pyrimidine with the structure (VI) was described by Menze, Clegg and Smart⁶ in 1952. This could be shown to be identical in all respects with the acetonitrile product. It was also observed (in Oslo) that chloroacetonitrile, bromoacetonitrile, and benzoyloxyacetonitrile gave 2-substituted 4-chloro-6-hydroxypyrimidines with malonyl chloride, (V), (III), and (VIII), respectively. The compounds analysed correctly and had NMR-spectra in complete accordance with the pyrimidine structures.

Five of the investigated nitriles, viz. butyro-, acetoxyaceto-, *p*-methoxyphenylaceto-, *p*-chlorophenylaceto-, and *p*-nitrophenylacetonitrile gave the 2-chloro-4,6-dihydroxypyrimidines (XI) to (XV).

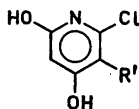
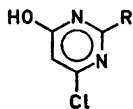
The pyrimidines (I), (III), (IV), (VI), are formed in yields ranging from 30 to 65 % containing no mixture with corresponding pyridines, although there are other by-products. Likewise, many of the pyridine products are obtained free from the corresponding pyrimidines. Only in a few cases have mixtures resulted, so far. Of mechanistic significance is the fact

that by increasing the ionic strength of the reaction mixture (addition of lithium perchlorate), chloroacetonitrile and benzoyloxyacetonitrile give the pyridines (IX) and (XVI), free from pyrimidines.

The stoichiometry of the pyrimidine synthesis can be formulated as follows:



The involvement of two molecules of nitrile is obvious and indeed the best yields were obtained with the proportions of the reactants indicated by the above scheme. The formation of an acid chloride containing the nitrile residue could be proved by GLC in the case of acetonitrile and chloroacetonitrile, and in the latter case by the isolation of chloroacetanilide after the filtrate from the reaction mixture had been treated with aniline. Experiments (at Surrey) involving ^{14}C labelling showed that carbon atoms 4, 5, and 6 of the pyrimidine products derive from the malonyl chloride (as expected) and that all of the carbon atoms of the acid chloride byproduct derive from the original nitrile. A mechanism is being proposed in an account of the work at Surrey, to be published elsewhere, and further studies are being made in Oslo, to be reported later.



- (I) R = CH_2F
 (III) R = CH_2Br
 (IV) R = CH_2CHBr
 (V) R = CH_2Cl
 (VI) R = CH_3
 (VII) R = CH_3CH_2
 (VIII) R = $C_6H_5COOCH_2$
 (IX) R' = Cl
 (X) R' = CH_3
 (XI) R' = CH_2CH_3
 (XII) R' = CH_2COO
 (XIII) R' = $CH_2OC_6H_4$
 (XIV) R' = ClC_6H_4
 (XV) R' = $NO_2C_6H_4$
 (XVI) R' = C_6H_5COO

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