Multiple regression technique provided corrections to the salinity data according to the bulk densities of the media, and greatly improved the correlations with plant growth. Whilst the correction formulae used proved very satisfactory over the range of high salinities studied, it cannot be assumed that the same formulae would necessarily apply at lower salinities. Since the corrections apparently depend on the relation between bulk density and moisture retention, however, it should be possible to develop correction formulae applicable to all salinity levels. Such corrections would prove particularly useful for potting composts containing a high proportion of peat; many of the potting composts now in use have very low bulk densities, and difficulties arise in the interpretation of salinity data.

Saturation of the 2·5 : 1 soil extracts with calcium sulphate improved the correlation of soil salinity with plant growth, although differences in the calcium sulphate content of the plots had not been created deliberately. The benefit from including calcium sulphate was greater for extracts prepared by weight than by volume (Tables I and II).

The variability encountered among lettuce plants under saline conditions necessitated extensive repetition of the trials. It appears that lettuce grown under somewhat adverse conditions may reveal variability which would not show up under the more favourable conditions of a normal breeding programme.

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FUNGICIDAL ACTIVITY AND CHEMICAL CONSTITUTION

XIV.*—Preparation of 4-substituted 2,6-dinitrophenols

By DIANA M. FIELDGATE and D. WOODCOCK

Six 4-(1-phenylalkyl)-, eight 4-(1-cyclohexylalkyl)- and seven 4-(1-cyclopentylalkyl)-2,6-dinitrophenols were prepared for testing against powdery mildew of apple (caused by *Podosphaera leucotricha* (Ell. & Everh.) Salm.) and other fungi.

Introduction

Work by Kirby and his associates[1] and in this laboratory[2,3] showed that, in general, 4-substituted-2,6-dinitrophenols are more effective against apple mildew than the isomeric 2,4-dinitro compounds. The former are also much less phytotoxic, so much so that many could be used with safety as free phenols.[2,4,5] The high activity shown by 4-(1-ethylhexyl)- and 4-(1-propylpentyl)-2,6-dinitrophenols prompted the synthesis of analogues containing an α-substituent, other than an alkyl group, in the n-alkyl chain.[6]

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Experimental and Results

Infra-red spectra were determined for liquid films or Nujol mulls on a Perkin-Elmer Infracord Spectrophotometer, Model 237, and only those absorption bands which are significant for structural assignments or identification are noted.

Thin-layer chromatography

The systems used were Kieselgel G (light petroleum (b.p. 40–60°)–ether–formic acid 80 : 20 : 2) and Kieselgel G (benzene).

Plates were sprayed either with a solution of 4% ceric sulphate in 10 wt.-% sulphuric acid or with a saturated

solution of chromic acid in 50 wt.-% sulphuric acid, and were baked at 140°.

Grignard reaction

This was carried out by refluxing the appropriate carbonyl compound in benzene solution for 3 hours with the required alkyl or cycloalkyl magnesium halide (2–3 equivalents) prepared in anhydrous ether. The mixture was cooled, and decomposed by means of saturated aqueous ammonium chloride, the ethereal layer was washed with water, dried over anhydrous sodium sulphate, and the solvent was distilled off.

Dehydration

The crude carbinol from the Grignard reaction was heated at 120–125° with an equal weight of powdered fused potassium hydrogen sulphate for 1 hour. The mixture was cooled and the product was extracted with ether, the ethereal solution was washed with aqueous sodium hydrogen carbonate and dried, and the solvent was removed. If necessary the product was purified by elution from a Grade I alumina column with light petroleum (b.p. 60–80°) alone and then with the addition of 10% benzene.

Hydrogenation

A solution of the olefin in ethyl alcohol or tetrahydrofuran was shaken with 10% palladised charcoal in hydrogen at laboratory temperature and pressure until there was no further uptake of gas. Filtration of the solution and removal of the solvent left the product, purified if necessary by elution from a Grade I alumina column as above.

De-methylation

In early de-methylation experiments, the use of hydrobromic acid (*d*, 1·48) or hydriodic acid (*d*, 1·9) at reflux temperatures either alone or with the addition of acetic acid or sulpholane was found to cause some fission of the 4-substituent with the formation of phenol. The method of Prey,[7] in which the methyl ether was refluxed for 3 h with an excess of pyridine hydrochloride was satisfactory, but preparation and manipulation of this hygroscopic reagent was tedious. More recently the use of pyridine and hydrochloric acid[8] has proved satisfactory. In all cases the cooled mixture was diluted with water and extracted with ether, the extract was washed free of pyridine with dilute hydrochloric acid, then with water and dried (Na_2SO_4). Removal of the solvent left the phenol, which if solid was crystallised to constant m.p. before nitration, but completeness of de-methylation was always checked using t.l.c. (System 1). For higher members of the series which tended to give a two-phase mixture, refluxing was necessary for a much longer period to ensure complete de-methylation.

Di-nitration

Method (a) (Two-stage)

Mono-nitration was carried out by the method of Jones.[9] A solution of the phenol (1 g) in chloroform (5 ml) was cooled and treated below 0° with a two-fold excess of nitric acid (*d*, 1·42) added dropwise with stirring. After 1·5 h, at laboratory temperature water was added, the chloroform layer separated, washed with water and dried ($CaCl_2$). Removal of the solvent gave the mononitrophenol which was examined by t.l.c. (System 1: yellow spot enhanced by ammonia vapour) and if not pure it was eluted from a Grade II alumina column using benzene, followed by benzene to which 1% ethanol had been added to promote 'banding'. Di-nitration was carried out by stirring a solution of the mononitro compound (1·5 g) in chloroform (6 ml) with a two-fold excess of nitric acid (*d*, 1·42) at 45° for 2 hours. The mixture was poured on to ice and the product isolated as before. It was examined by t.l.c. (System 1: orange spot enhanced by ammonia vapour) and if necessary purified as before, the addition of 0·1–0·2% acetic acid to the benzene–ethanol mixture being necessary in this case to promote 'banding' and to make removal of the dinitrophenol possible.

Method (b) (Single stage)

In both 4-(1-cycloalkylalkyl)-phenol series, nitration was carried out by dropwise addition of a solution of the phenol in glacial acetic acid (3 parts) to a stirred mixture of nitric acid (*d*, 1·5, 2 mol) and glacial acetic acid (2 parts), the temperature being kept below 30°. After standing overnight at laboratory temperature, the mixture was poured on to ice and extracted with ether, the extract was washed with water, then sodium hydrogen carbonate solution and then dried (Na_2SO_4). Removal of the solvent gave the dinitro compound which was examined and purified as described above, solid products being recrystallised to constant m.p.

2,6-Dinitro-4-(1-phenylalkyl)phenols

1-(p-*Methoxyphenyl*)-1-*phenylprop*-1-*ene*

4-Methoxybenzophenone (17 g) in dry benzene (50 ml) was added dropwise to a cooled solution of ethyl magnesium iodide, prepared from magnesium (5·5 g) and ethyl iodide (13·7 g) and then refluxed for 1·5 h. The red-brown product (21 g) isolated as described above showed no sign of the original ketone (t.l.c. System 2; no C = 0 peak at 1648 cm^{-1}), and absence of any absorption in the 3100–3600 cm^{-1} region indicated that spontaneous dehydration of the carbinol had occurred. After several crystallisations from ethyl alcohol it had m.p. 53–54°. (Found: C, 85·3; H, 7·1; $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%).

1-(p-*Methoxyphenyl*)-1-*phenylpropane*

A solution of the above solid (7 g) in tetrahydrofuran (80 ml) was shaken with palladised charcoal (0·7 g) in hydrogen at laboratory temperature and pressure until there was no further uptake of gas (~2 h). Filtration of the solution and removal of the solvent gave an oil (8·1 g), purified by elution from a short Grade I alumina column.

4-(1-*Phenylpropyl*) *phenol*

The above methoxy compound (7 g), de-methylated using pyridine hydrochloride as already described, gave a pale yellow oil (6 g) which showed only a single spot of lower R_f than the corresponding methyl ether (t.l.c., System 2). ν_{max} 3350, 1240 cm^{-1} (OH bands) replacing peaks at 2840, 1250 cm^{-1} (OCH_3.)

2-*Nitro*-4-(1-*phenylpropyl*) *phenol*

The above phenol (6 g) was mono-nitrated by method (a). The product was a yellow oil which, crystallised from light petroleum (b.p. 40–60°), had m.p. 41·5–43° (Found: C, 69·6; H, 5·5; N, 5·5. $C_{15}H_{14}NO_3$ requires C, 70·0; H, 5·8; N, 5·45%). ν_{max} (cm^{-1}) 3245 (bonded OH), 1538 (NO_2).

2,6-*Dinitro*-4-(1-*phenylpropyl*) *phenol*

A solution of the above mononitrophenol (1·5 g) on further nitration (Method a) gave an orange-coloured oil (0·5 g), purified by elution from Grade II alumina. (Found: C, 60·4; H, 4·6; N, 9·0. $C_{15}H_{14}N_2O_5$ requires C, 59·6; H, 4·6; N, 9·3%). ν_{max} (cm^{-1}) 3200 (strongly bonded OH), 1538 (NO_2).

Four other new 2,6-dinitro-4-(1-phenylalkyl) phenols, which were all yellow oils, were similarly prepared by way of the corresponding mononitro-compounds. The product at each stage was examined by t.l.c. and by infra-red spectroscopy for purity and identity. The following were prepared:

2,6-*Dinitro*-4-(1-*phenylethyl*) *phenol*, 60% yield (based on original ketone). (Found: N, 9·9%. $C_{14}H_{12}N_2O_5$ requires N, 9·7%).

2,6-*Dinitro*-4-(1-*phenyl-n-butyl*) *phenol**, 10% yield. (Found: N, 9·0. $C_{16}H_{16}N_2O_5$ requires N, 8·9%).

2,6-*Dinitro*-4-(1-*phenyl-n-pentyl*) *phenol*, 55% yield. (Found: N, 8·6. $C_{17}H_{18}N_2O_5$ requires N, 8·5%).

2,6-*Dinitro*-4-(1-*phenyl-n-hexyl*) *phenol*, 50% yield. (Found: N, 8·1. $C_{18}H_{20}N_2O_5$ requires N, 8·1%).

The isolation and identification (mixed m.p. with an authentic specimen) of 4-benzyl-2,6-dinitrophenol (m.p. 86°) in the final product, when earlier stages had not been rigorously purified by elution from an alumina column, showed that two-electron reduction of the 4-methoxybenzophenone by the Grignard reagent could take place to some extent.

2,6-Dinitro-4-(1-cyclohexylalkyl) phenols

1-(p-*Methoxyphenyl*)-1-*cyclohexylpent*-1-*ol*

A solution of cyclohexyl magnesium bromide prepared from magnesium (1 g) and cyclohexyl bromide (5·5 ml) was cooled to 0° and stirred during the dropwise addition of a solution of 4-methoxyphenyl butyl ketone (3·9 g) in dry benzene (14 ml), and then refluxed for 3 hours. The product, isolated as usual, was a pale yellow oil (9·2 g) showing a medium OH peak (ν_{max} 3480 cm^{-1}).

1-(p-*Methoxyphenyl*)-1-*cyclohexylpent*-1-*ene*

The above oil (9·2 g) was dehydrated as previously described and the brown oily product (6·7 g) was purified using an alumina column (Grade I). Dicyclohexyl (0·42 g) was eluted first by means of light petroleum (b.p. 60–80°) (ν_{max} 2920, 2850, 2450, 1000, 995 cm^{-1}).[10,11] Subsequent elution with light petroleum (b.p. 60–80°) containing 10% benzene gave the olefin (3·8 g) which showed a single spot (t.l.c., System 2) and complete disappearance of the band at 3480 cm^{-1}.

1-(p-*Methoxyphenyl*)-1-*cyclohexyl-n-pentane*

The above olefin (3·8 g) reduced catalytically gave a colourless oil (3·8 g) which showed only a single spot of higher R_f than the olefin (t.l.c., System 2).

4-(1-*Cyclohexyl-n-pentyl*) *phenol*

The above methoxy pentane (3·8 g), de-methylated using pyridine hydrochloride, gave a solid (3·6 g) which after several crystallisations from light petroleum (b.p. 60–80°) had m.p. 112–113°. (Found: C, 82·7; H, 11·0. $C_{17}H_{26}O$ requires C, 82·9; H, 10·6%) ν_{max} 3300 cm^{-1} (OH broad band), 1320 (OH peak, replacing band at 1250).

4-(1-*Cyclohexylpentyl*)-2,6-*dinitrophenol*

A solution of the above phenol (2·9 g) was nitrated in glacial acetic acid as previously described (Method b). The product was a yellow oil (3·9 g, 75% yield based on original ketone) which was purified by elution from a Grade II alumina column. The i.r. spectrum was typical of a 2,6-dinitro-4-substituted phenol (ν_{max} 3180, 1550 cm^{-1}—strongly bonded OH and NO_2 respectively). (Found: N, 8·1. $C_{17}H_{24}N_2O_5$ requires N, 8·3%). Other members of this series, which were yellow oils where no m.p. is given, were prepared similarly, the intermediates involved being checked for purity and identity by t.l.c. and infra-red spectroscopy before proceeding to the next stage. The following were prepared:

4-(1-*Cyclohexylmethyl*)-2,6-*dinitrophenol** was crystallised from aqueous methanol, m.p. 72–73° in 75% yield. (Found: N, 10·0. $C_{13}H_{16}N_2O_5$ requires N, 10·0%). 4-(1-*Cyclohexylethyl*)-2,6-*dinitrophenol* was crystallised from light petroleum (b.p. 40–60°) m.p. 51–52° in 70% yield. (Found: N, 10·0. $C_{14}H_{18}N_2O_5$ requires N, 9·5%). 4-(1-*Cyclohexyl-n-propyl*)-2,6-*dinitrophenol* was crystallised from light petroleum (b.p. 40–60°), m.p. 62–63° in 50% yield. (Found: N, 9·5. $C_{15}H_{20}N_2O_5$ requires N, 9·1%). 4-(1-*Cyclohexyl-n-butyl*)-2,6-*dinitrophenol* gave 50% yield. (Found: N, 8·2. $C_{16}H_{22}N_2O_5$ requires N, 8·7%), and 4-(1-*Cyclohexyl-n-hexyl*)-2,6-*dinitrophenol*, 80% yield. (Found: N, 7·9. $C_{18}H_{26}N_2O_5$ requires N, 8·0%). 4-(1-*Cyclohexyl-n-heptyl*)-2,6-*dinitrophenol* gave 50% yield. (Found: N, 7·8 $C_{19}H_{28}N_2O_5$ requires N, 7·7%) and 4-(1-*Cyclohexyl-n-octyl*-2,6-*dinitrophenol*, 50% yield. (Found: N, 7·7 $C_{20}H_{30}N_2O_5$ requires N, 7·4%).

2,6-Dinitro-4-(1-cyclopentylalkyl) phenols

4-(*Cyclopentylmethyl*) *anisole*

An ethyl alcoholic solution of *p*-methoxyphenyl cyclopentyl ketone (1 g), prepared according to a method of Hey & Musgrave,[12] was shaken with 10% palladised charcoal (0·1 g) in hydrogen at laboratory temperature and pressure until there was no further uptake of gas. Removal of the solvent from the filtered solution left a colourless oil (1 g) which showed complete absence of a peak at 1670 cm^{-1} (C = O).

4-*Cyclopentylmethyl phenol*

De-methylation of the above anisole (1 g) using pyridine and hydrochloric acid[8] gave a light brown oil (0·8 g) showing only a single spot (t.l.c., System 2). (ν_{max} 3320, 1255 cm^{-1}).

2,6-*Dinitro*-4-*cyclopentylmethyl phenol*

The above phenol (0·8 g) was di-nitrated and the product (1·1 g) was isolated by method (b). It was purified by graded elution from an alumina column (Grade II) using successively benzene, benzene + 1% ethanol, benzene + 2% ethanol + 0·2% acetic acid, to give a yellow oil produced in 75% yield. (Found: N, 10·5. $C_{12}H_{14}N_2O_5$ requires N, 10·5%). (ν_{max} cm^{-1} 3190 (strongly bonded OH), 1530–1550 (NO_2))

* Prepared by Mr. D. R. Clifford

* Prepared by Mr. E. D. Evens

Reaction of cyclopentylmagnesium bromide with 4-methoxyphenylpropyl ketone

A solution of cyclopentyl magnesium bromide, prepared from magnesium (2·2 g) and cyclopentyl bromide (11 ml) in anhydrous ether, was cooled to 0° and stirred during the dropwise addition of 4-methoxyphenylpropyl ketone (8 g) dissolved in dry benzene (28 ml). After reflux for 3 h the mixture was processed as described earlier. The product was a brown oil (10·7 g) which showed two major low R_f spots when examined by t.l.c. (System 2). This oil was dehydrated using potassium hydrogen sulphate (10·7 g) as already described, and distillation of the product gave two fractions (A) 5·8 g, b.p. 145–150°/20mm and (B) 1·1 g, b.p. ~200°/20mm. Each fraction was catalytically hydrogenated and the products were de-methylated as already described. The phenol from fraction (A) had an i.r. spectrum almost identical with that of 4-n-butylphenol. Nitration (Method b) gave a yellow dinitro derivative which showed an orange-coloured spot of the same R_f value as 4-n-butyl-2,6-dinitrophenol (t.l.c. System 1). After several recrystallisations from light petroleum (b.p. 40–60°) it had m.p. 43–45°, which was not depressed by admixture with an authentic specimen. A study of the C-H str. (2800–3000 cm^{-1}) and C-H def. (1310–1370, 1440–1470 cm^{-1}) regions of the i.r. spectrum of the phenol from fraction (B), indicated the presence of the cyclopentyl group. Nitration (Method b) gave an orange-coloured oil which showed two orange spots using t.l.c. (System 1), the R_f of the smaller of these being the same as that of 4-n-butyl-2,6-dinitrophenol. The mixture was purified by column chromatography using Kieselgel (0·05–0·2 mm, activated at 120°) and elution with light petroleum (b.p. 60–80°) followed by that solvent mixed with an increasing proportion of benzene. Crystallised from light petroleum (b.p. 40–60°) it had m.p. 53–54.° (Found: N, 9·3. $C_{15}H_{20}N_2O_5$ requires N, 9·1%).

1-(p-*Methoxyphenyl*)-1-*cyclopentylbut*-1-*ene*

A solution of propylmagnesium bromide prepared from magnesium (4·8 g) and n-propyl bromide (20 ml) in anhydrous ether was cooled to 0° and stirred during the dropwise addition of a solution of *p*-methoxyphenyl-cyclopentyl ketone (20·4 g) in dry benzene (70 ml). After reflux for 3 h the mixture was processed as described earlier and the resultant oil (28·9 g) was dehydrated as usual. The product (26·1 g) was a light brown oil showing no absorption at 1675 cm^{-1} (C = O) and 3100–3600 cm^{-1} (OH) in the i.r. spectrum, and a single spot of different R_f from the original ketone (t.l.c. System 2).

4-(1-*Cyclopentylbutyl*) *phenol*

The above olefin (25 g) was catalytically hydrogenated, and the resultant 4-cyclopentylbutyl anisole was de-methylated using pyridine and hydrochloric acid as previously described. The product (18·6 g) showed only a single spot (t.l.c. System 2) and after several recrystallisations from light petroleum (b.p. 60–80°) had m.p. 77–78°. (Found: C, 82·4; H, 10·4. $C_{15}H_{22}O$ requires C, 82·5; H, 10·1%).

2,6-*Dinitro*-4-(1-*cyclopentylbutyl*) *phenol*

The above phenol (11·9 g) was nitrated (Method b) and the product (15·8 g) was isolated as previously described. It crystallised from light petroleum (b.p. 40–60°) (charcoal) and had m.p. 54–55°, yield 60% (overall). (Found: N, 9·3. $C_{15}H_{20}N_2O_5$ requires N, 9·1%). The following analogues were prepared in a similar way:

2,6-*Dinitro*-4-(1-*cyclopentylethyl*) *phenol* was crystallised from light petroleum (b.p. 40–60°) (charcoal) and had m.p. 45–46° (Found: N, 9·6. $C_{13}H_{16}N_2O_5$ requires N, 10·0%) 50% yield, based on *p*-methoxyphenyl cyclopentyl ketone.

2,6-*Dinitro*-4-(1-*cyclopentylpropyl*) *phenol* was crystallised from light petroleum (b.p. 40–60°) and had m.p. 76–77° (64% yield overall). (Found: N, 9·5. $C_{14}H_{18}N_2O_5$ requires N, 9·5%).

2,6-*Dinitro*-4-(1-*cyclopentylpentyl*) *phenol* was an orange-coloured oil prepared in 50% yield and purified by elution from an alumina column (Grade II). (Found: N, 9·0. $C_{16}H_{22}N_2O_5$ requires N, 8·7%).

2,6-*Dinitro*-4-(1-*cyclopentylheptyl*) *phenol* was an orange-coloured oil, purified as for the pentyl analogue (50% yield). (Found: N, 8·3. $C_{18}H_{26}N_2O_5$ requires N, 8·0%).

2,6-*Dinitro*-4-(1-*cyclopentylhexyl*) *phenol* was only prepared by reaction of *p*-methoxyphenyl n-pentyl ketone and cyclopentyl magnesium bromide, successive dehydration and hydrogenation of the product yielding a mixture of 4-n-hexylanisole and 4-(1-cyclopentylhexyl) anisole. These were separated on an Autoprep A 700 gas chromatograph, the 10 ft × ⅜ in. o.d. copper column being packed with acid-washed Chromosorb G coated with LAC-2R-446 (2·5%) and orthophosphoric acid (0·2%) and run at 215° during the passage of helium at 150 ml min^{-1}. The cyclopentyl compound, which had the longest retention time, was collected, de-methylated and nitrated (Method b). The dinitro derivative produced in 10% overall yield was an orange coloured oil. (Found: N, 7·9. $C_{17}H_{24}N_2O_5$ requires N, 8·3%.)

Discussion

Members of the 2,6-dinitro-4-(1-phenylalkyl) phenol series were conveniently prepared from the commercially available *p*-hydroxybenzophenone. After methylation, introduction of the alkyl group was effected by the normal 1,2- addition of the appropriate alkyl magnesium halide, followed by dehydration, reduction and de-methylation. In the last stage, hydrobromic or hydriodic acids could not be used either in acetic acid or in sulpholane because of breakdown leading to phenol formation, and hydrochloric acid was preferred. One-stage di-nitration of the de-methylated product also lead to a certain amount of fission, with the formation of 2,4-dinitrophenol and picric acid, but this difficulty was resolved by a preliminary mono-nitration in chloroform solution.

p-Hydroxyphenylalkyl ketones, prepared by Fries reaction from the corresponding phenyl esters, were the starting materials for the synthesis of the 4-(1-cyclohexylalkyl) phenols. Reaction with cyclohexylmagnesium bromide was essentially by a normal 1,2- addition, though a small amount of dicyclohexyl was formed—presumably as a result of one-electron reduction of the carbonyl group leading to pinacol formation.[13] Often the resultant carbinols underwent dehydration during processing, but the subsequent reaction sequence was the same as in the phenylalkyl series, except that single-stage di-nitration was possible in this case. An analogous use of cyclopentylmagnesium bromide for the preparation of 4-(1-cyclopentylalkyl) phenols, however, could not be made since with this Grignard reagent, two-

electron reduction of the *p*-methoxyphenylalkyl ketone takes precedence over the normal 1,2- addition process (cf. Hey & Musgrave,[12] Kharasch & Weinhouse.[14]). Separation of the cyclopentylalkyl from the n-alkyl derivative at any subsequent stage of the reaction sequence proved very tedious, although 4-(1-cyclopentylhexyl) anisole has been separated relatively easily from 4-n-hexyl anisole by preparative gas–liquid chromatography. This series was therefore more conveniently prepared starting with *p*-methoxyphenylcyclopentyl ketone, reaction with various alkyl magnesium halides being followed by a procedure analogous to that used on the phenylalkyl series.

Tested at various concentrations for the ability to protect apple seedlings against mildew caused by *Podosphaera leucotricha* many of the compounds, particularly some members of the two cycloalkyl series, proved highly active. Results of the tests with this and other fungi have still to be published.

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SENSORY AND OBJECTIVE MEASUREMENTS OF THE QUALITY OF FROZEN STORED COD OF DIFFERENT INITIAL FRESHNESSES

By J. J. CONNELL and P. F. HOWGATE

The eating quality of cod kept for different periods in melting ice before being frozen and stored at three different temperatures has been evaluated by a taste panel using a new score sheet. Objective measurements of both initial freshness before freezing and deterioration during frozen storage were carried out on the same samples. Correlations were obtained between the objective measurements and various aspects of eating quality. The relative contributions of the various aspects of eating quality to the final overall acceptability were obtained, and the value of the objective measurements in predicting overall acceptability assessed.

Introduction

Between the time a fish is caught and it is eaten after being frozen, it will have undergone a complex and often variable series of temperature changes each occurring over a different time interval. In general, the temperature history of the fish will include the following phases: unfrozen storage, freezing, frozen storage, thawing, storage in the thawed state. In some types of product the freezing–thawing phase may occur more than once. During each of these phases the fish may change in ways which will adversely affect its acceptability as an article of food. These changes are of three kinds, spoilage due to microbiological action, changes due to the action of endogenous enzymes, and chemical or physical changes such as oxidation or loss of flavour components through leaching or 'weeping'. All three kinds of change can occur during the unfrozen storage phases, whilst