

CONTENTS

HETEROCYCLIC COMPOUNDS

(continued)

LIST OF PERIODICALS	VII
OFFICIAL PUBLICATIONS	XXVII
LIST OF COMMON ABBREVIATIONS AND SYMBOLS USED	XXV

*Chapter VIII. Compounds Containing a Six-Membered Ring with
One Hetero Atom, Oxygen or Sulphur*

by NEIL CAMPBELL

Introduction	809
1. Pyran and its Derivatives	810
a. Pyrans, Pyranols and Pyrones	810
(i) α - and γ -Pyrans, 810 - (ii) Pyranols, 811 - (iii) Pyrylium Salts, 811 - (iv) α - and γ -Pyrones, 814 [a-Pyrones, 815 - Methods of Preparation, 815 - Properties, 817 - γ -Pyrones, 821 - Constitution and Fine Structure, 821 - Methods of Preparation, 822 - Properties, 823] - (v) Hydroxy- γ - pyrones, 828 - (vi) γ -Pyronecarboxylic Acids, 832	810
b. Dihydropyrans and their Oxidation Products	835
(i) 2:3-Dihydro- γ -pyran, 835 - (ii) 5:6-Dihydro- α -pyran, 837 - (iii) Naturally Occurring Furodihydropyran Derivatives, 837	835
c. Tetrahydropyran and Derivatives	839
2. 5:6-Benzopyrans (Chromens) and their Derivatives	841
a. Chromens and their Oxidation Products	842
(i) Chromens. Alkyl- and Aryl-chromens, 842 - (ii) Chromenols (5:6-Benzopyranols), 846 [(iia) Benzopyrylium or Chromylum Salts, 847: Methods of Synthesis, 847 - Fine Structure of the Benzopyrylium Salts, 850 - Properties, 850 - (iib) The Anthocyanins and Anthocyanidins, 855: Methods of Synthesis, 859 - (iic) Leucoanthocyanins, 867] - (iii) Coumarin (5:6-Benzo- α -pyrone) and its Derivatives, 869 [Synthesis, 869 - Properties, 872 - (iiia) Coumarin, Alkyl- and Aryl-coumarins, 875 - (iiib) Hydroxycoumarins, 878 - (iiic) Naturally Occurring Coumarin Deriva- tives, 880: (1) Naturally Occurring Hydroxycoumarins, 881 - (2) Furo- coumarins, 883 - (3) Coumarins Containing a Fused 2:a-Dimethyl- chromen Nucleus, 887] - (iv) Chromones (5:6-Benzo- γ -pyrones), 888 [Methods of Synthesis, 889 - Structure and Properties, 893 - (iva) Chro- mone, Alkylchromones and Hydroxychromones, 897 - (ivb) Naturally Occurring Chromones, 898: (1) Hydroxychromones, 898 - (2) Furochro- mone, 900 - (3) Pyranochromones, 902 - (ivc) Flavones (2-Phenylchro-	842

mones), 903 - (ivd) Flavonols (<i>3</i> -Hydroxyflavones), 906 - (ive) Flavone and Flavonol Pigments, 907: Synthesis, 908 - Hydroxyflavones with no <i>3</i> -Hydroxyl Group, 910 - Hydroxyflavones with a <i>3</i> -Hydroxyl Group; Hydroxyflavonols, 914 - Euroflavones, 920 - (ivf) <i>iso</i> Flavones (<i>3</i> -Phenylchromones), 921: Naturally Occurring <i>iso</i> Flavones, 924]	
b. Chroman (Dihydrochromen) and Derivatives	927
(i) Chromans, 927 - (ii) Naturally Occurring Chromans, 928 [Tocopherols, 928 - Structure, 929 - Properties, 931] - (iii) Phenylchromans (Flavan and <i>iso</i> Flavan), 932 - (iv) Chromanol, 934 - (v) Flavanols: the Catechins and Related Condensed Tannins, 935 [Catechins, 935 - Condensed Tannins, 940] - (vi) Chromanones, 942 [Chromanochromanones. Rotenone and Related Substances, 944] - (vii) Flavanones, 2-Phenylchroman-4-ones, 954 - (viii) Hydroxyflavanones, 956 - (ix) <i>iso</i> Flavanones, 3-Phenylchroman-4-ones, 961	
3. <i>iso</i> Benzopyran (<i>3</i> : <i>4</i> -Benzopyran) and its Derivatives	961
a. <i>iso</i> Coumarins	962
b. <i>iso</i> Chroman and Derivatives	965
4. Xanthan (<i>2</i> : <i>3</i> - <i>5</i> : <i>6</i> -Dibenzopyran) and its Derivatives	966
a. Xanthen, Alkyl- and Aryl-xanthens	966
b. Xanthhydrols and Xanthen Colouring Matters	969
(i) Fluorones and Fluorimes, 970 - (ii) Xanthen Dyes, 971 [(1) Pyronines, 972 - (2) Rosamines and Rhodamines, 973 - (3) Fluorescein and Related Compounds, 974]	
c. Xanthones	976
Methods of Synthesis, 976 - (i) Halogenoxanthones, 978 - (ii) Nitro- and Amino-xanthones, 979 - (iii) Hydroxyxanthones, 980	
5. 3: <i>4</i> -Benzochromen and its Derivatives	983
6. 5: <i>6</i> -Benzochromens and their Derivatives	984
7. 6: <i>7</i> -Benzochromens and their Derivatives	985
8. 7: <i>8</i> -Benzochromens and their Derivatives	986
g. Benzo- and Dibenzo-xanthen Derivatives	987
IO. Thiapyran Derivatives	988
a. Thiapyrans and Thiapyrones	988
b. Hydrogenated Thiapyrans and Thiapyrones	989
(i) Dihydrothiapyrans, 989 - (ii) Tetrahydrothiapyrans, 990	
II. Thiachromens (<i>5</i> : <i>6</i> -Benzothiapyrans) and Derivatives	992
a. 5: <i>6</i> -Benzothiapyrans and 5: <i>6</i> -Benzothiapyrones	992
(i) Thiachromens, 992 - (ii) Thiacoumarins, 993 - (iii) 1-Thiachromones and 1-Thiaflavones, 993	
b. Thiachromans and Thiachromanones	994
12. Dibenzothiapyran (Thiaxanthen) and Derivatives	997
13. <i>iso</i> Thiachromen (<i>3</i> : <i>4</i> -Benzothiapyran) and Derivatives	1001
a. <i>iso</i> Thiachromen and <i>iso</i> Thiacoumarins	1001
b. <i>iso</i> Thiachroman and Derivatives	1001
14. Bridged Ring Sulphur Compounds	1002

Chapter IX. Brazilin and Haematoxylin

by Sir ROBERT ROBINSON

I. The Brazilin Group	1005
[Oxidation of O-Trimethylbrazilin by Means of Permanganate, 1007 - Oxidation of O-Trimethylbrazilin by Means of Chromic Acid in Acetic	

Acid Solution, 1009 - Brazilein and its Derivatives, 1013 - The <i>iso</i> -Brazilein or Braziylum Salts, 1016 - Synthesis of Braziylum and Other Indenobenzopyrylium Salts, 1017 - Synthesis of Deoxytrimethylbrazilone and Trimethylbrazilone, 1018 - The Constitution of Brazilein, 1019 - Synthesis of Braziulin, 1020]	
2. The Haematoxylin Group	1021
[Permanganate Oxidation of <i>d</i> -Tetramethylhaematoxylin, 1021 - Haematin and its Derivatives, 1022 - Possible Natural Occurrence of a Haematoxylin Methyl Ether, 1023 - Optical Rotatory Powers of Brazilin and Haematoxylin and their Derivatives, 1023]	

Chapter X. Compounds Containing Two Fused Five- or Six-Membered Heterocyclic Rings Each of One Hetero Atom

by NEIL CAMPBELL

1. Compounds Containing Two Hetero Rings Fused to an Aromatic System	1024
a. Pyranoquinolines	1024
b. Bz-Pyrroloquinolines	1025
c. Phenanthrolines	1026
d. Dipyridonaphthalenes	1027
2. Compounds Containing Two Hetero Rings Fused Through Adjacent Carbon Atoms	1028
a. Furanoquinolines	1028
b. Pyranoquinolines	1030
c. Pyrrolopyridines or Diazaindenes	1031
[Carbolines, 1033 - Indoloquinolines or Quinindolines, 1034]	
d. Naphthyridines or Pyridopyridines	1035
3. Fused Heterocyclic Systems Having a Nitrogen Atom Common to Two Rings	1038
a. Pyrrocolines	1038
b. Pyridocolines	1041
[Norlupinane and Lupinane, 1042]	
c. Julolidine and Lilolidine	1046
4. Bridged Ring Compounds	1048
a. Compounds with Nitrogen Common to Two Rings	1048
b. Bicyclic Systems Having a Nitrogen Bridge	1051

Chapter XI. The Cyanine and Related Dyes

by G. DE W. ANDERSON

Introduction	1053
1. Cyanines	1054
Historical, 1054 - Methods of Preparation, 1056 [(i) Monomethincyanines, 1056 - (ii) Trimethincyanines, 1058 - (iii) Meso-substituted Unsymmetrical Trimethincyanines, 1060 - (iv) Symmetrical Trimethincyanines with Miscellaneous Chain Substituents, 1061 - (v) Penta- and Higher Poly-methincyanines, 1062] - Properties of the Cyanine Dyes, 1064 - Typical Compounds, 1066	

2. Azacyanines	1068
3. Neocyanines and Related Dyes	1069
4. Merocyanines	1071
Methods of Preparation, 1072 - Properties of the Merocyanine Dyes, 1074 - Typical Compounds, 1075	
5. Linear Tri- and Poly-nuclear Cyanines and Merocyanines	1075
Properties, 1076 - Typical Compounds, 1077	
6. Oxonol Dyes.	1078
7. Styryl Dyes and N-Hemicyanines	1079

Chapter XII. The Indigo Group

by T. S. STEVENS

Introduction	1081
I. Indigo (Indigotin) and its Derivatives	1083
Constitution, 1083 - Synthetic Methods, 1085 - Properties. 1087 - (i) N-Derivatives of Indigo, 1089 - (ii) Derivatives of the Carbonyl Function, 1091 - (iii) Homologues of Indigo, 1091 - (iv) Halogeno-indigos, 1092 - (v) Other Substituted Indigos, 1092 - (vi) Dehydroindigo, 1093 - (vii) Indigo-white, 1094 - (viii) Polycyclic Indigos, 1094	
2. Indirubin	1095
3. isoIndigo	1097
4. Other Indigoid Pigments	1098
a. Thioindigos	1098
b. Thionaphthenindoleindigos	1102
c. Vinylene Homologues of the Indigos	1103

Chapter XIII. The Pyrrole Pigments

by T. S. STEVENS

Introduction	1104
I. Linear Pigments	1105
a. Dipyrromethenes and Related Compounds	1105
Methods of Synthesis, 1105 - (i) Simple Dipyrromethenes, 1107 - (ii) Hydroxydipyrromethenes or their Tautomerides, 1109 - (iii) Tri- and Poly-nuclear Systems, 1110	
b. Bile Pigments (Bilirubinoids)	1111
Nomenclature, 1112 - Synthetic Methods, 1114 - (i) Bilitrienes, 1114 - (ii) Bilidenes, 1115 - (iii) Bilenes and Bilans, 1118 - (iv) Diagnostic Reactions, 1118	
2. Macrocyclic Pigments: Unreduced Porphins	1119
Synthetic Methods, 1120 - General Properties, 1122	
a. Porphin and its Simple Derivatives	1124
b. Porphinpropionic Acids	1126
c. Haemoglobin	1128
(i) Structure of Protoporphyrin and Haemin, 1128 - (ii) Haemoglobin: Properties and Transformations, 1130	
d. Other Porphyrin-Protein Complexes	1131
e. Naturally Occurring Protein-free Porphyrins	1133

3. Reduced Porphins. Chlorophyll	1134
a. Synthetic Reduced Porphins	1134
(i) Dihydroporphins, 1134 - (ii) Tetra-, Hexa-, and Octa-hydroporphins, 1138	
b. Chlorophyll	1139
Nomenclature, 1140 - (i) Structure and Reactions of Chlorophyll-a, 1140 [The Porphin Skeleton, 1140 - The Homocyclic Ring, 1142 - The Vinyl Group, 1143 - The Phorbide-Porphyrin Relationship, 1143 - The "Extra" Hydrogen Atoms: Location, 1144 - Other Transformations of Chlorophyll-a, 1145] - (ii) Chlorophyll-b, 1146 - (iii) Absorption Spectra of Phorbides and Chlorins, 1147 - (iv) Bacteriochlorophyll, 1149	
c. Biosynthesis of Porphyrins	1149
d. Vitamin B ₁₂ (Cyanocobalamine)	1151
4. Aza- and Benzo-porphins; Phthalocyanines	1154
a. Azaporphins	1155
(i) Monoazaporphins, 1155 - (ii) Diazaporphins, 1155 - (iii) Tetraaza-porphins, 1156	
b. Benzoporphins and Benzoazaporphins	1156
Synthetic Methods, 1157 - (i) Tetrabenzoporphin, 1158 - (ii) Tetrabenzo-mono-, -di-, and -tri-aza-porphins, 1158 - (iii) Tetrabenztetraaza-porphins (Phthalocyanines), 1159 - (iv) Macrocyclic Systems Related to Phthalocyanine, 1162	

Chapter XIV. Compounds Containing Unusual Hetero Atoms

by (Miss) I. G. M. CAMPBELL and (in part) T. S. STEVENS

1. Five Membered Rings with One Hetero Atom	1163
a. Silicon Compounds	1163
b. Phosphorus Compounds	1164
c. Arsenic Compounds	1166
d. Antimony Compounds	1168
e. Halogen Compounds	1169
2. Five Membered Rings with more than One Hetero Atom	1170
a. Five Membered Rings Containing Silicon and Oxygen or Sulphur	1170
b. Five Membered Rings Containing Phosphorus and Oxygen or Nitrogen	1170
c. Five Membered Rings Containing Arsenic and Oxygen	1171
d. Five Membered Rings Containing Arsenic and Sulphur	1173
e. Five Membered Rings Containing Antimony and Oxygen	1174
f. Five Membered Rings Containing Antimony and Sulphur	1174
g. Five Membered Rings Containing Bismuth and Oxygen or Sulphur	1175
3. Six Membered Rings Having One Hetero Atom	1176
a. Silicon Compounds	1176
b. Germanium, Tin and Lead Compounds	1177
c. Phosphorus Compounds	1178
d. Arsenic Compounds	1180
(i) Arsacyclohexanes, 1180 - (ii) Tetrahydroarsinolines, 1181 - (iii) Ars-acridines, 1183 - (iv) Arsaphenanthrenes, 1183 - (v) Arsaperinaphth-indane, 1184	
e. Antimony and Bismuth Compounds	1184
f. Iodine Compounds	1185

4. Six Membered Rings with more than One Hetero Atom	1186
a. Six Membered Rings Containing Silicon with Oxygen, Sulphur or Nitrogen	1186
b. Six Membered Rings Containing Phosphorus with Oxygen or Nitrogen	1189
c. Six Membered Rings Containing Arsenic with Oxygen, Sulphur or Nitrogen	1190
d. Six Membered Rings Containing Antimony and Oxygen	1193
e. Six Membered Rings Containing Two Phosphorus Atoms or Phosphorus and Arsenic	1194
f. Six Membered Rings Containing Two Arsenic Atoms	1195
5. Seven Membered and Larger Rings	1197
a. Silicon and Tin Compounds	1197
b. Phosphorus and Arsenic Compounds	1198
c. Larger Rings Containing Two Arsenic Atoms	1199
d. Iodine Compounds	1200
Bibliography	1200

*Chapter XV. Compounds Containing a Six Membered Ring
with Two Hetero Atoms. The Diazines*

by G. R. RAMAGE and (in part) J. K. LANDQUIST

1. The Pyridazine Group	1201
a. Pyridazine and its Substitution Products	1201
Methods of Synthesis, 1202 - (i) Pyridazine and its Alkyl and Aryl Derivatives, 1204 - (ii) Halogenopyridazines, 1205 - (iii) Aminopyridazines, 1205 - (iv) Hydroxypyridazines (Pyridazones), 1206 - (v) Pyridazinecarboxylic Acids, 1209	
b. Hydropyridazines	1211
(i) Dihydropyridazines, 1211 - (ii) Tetrahydropyridazines, 1215 - (iii) Hexahydropyridazines (Piperidazines), 1216 - Benzopyridazines, 1217	
c. Cinnoline and its Substitution Products	1217
Methods of Synthesis, 1217 - (i) Cinnoline and its Alkyl and Aryl Derivatives, 1218 - (ii) Reduced Cinnolines, 1220 - (iii) Halogenocinnolines, 1221 - (iv) Nitrocinnolines, 1222 - (v) Aminocinnolines, 1223 - (vi) Hydroxycinnolines, 1228 - (vii) Cinnolinecarboxylic Acids, 1232	
d. Benzo[c]cinnolines	1233
(i) Benzo[c]cinnoline and its Alkyl Derivatives, 1234 - (ii) Halogeno-, Nitro- and Other Substituted Benzo[c]cinnolines, 1235 - (iii) Reduced Benzo[c]cinnolines, 1237	
e. Other Benzocinnolines	1237
f. Phthalazines	1238
Methods of Synthesis, 1238 - (i) Phthalazine, its Alkyl and Aryl Derivatives, 1239 - (ii) Reduced Phthalazines, 1240 - (iii) Halogenophthalazines, 1241 - (iv) Aminophthalazines, 1242 - (v) Hydroxyphthalazines and Dihydrophthalazines, 1244 - (vi) Phthalazine Compounds from Benzenediazonium Salts of 2-Naphthol-1-sulphonic acid, 1253	
2. The Pyrimidine Group	1257
a. Pyrimidine (1:3-Diazine) and its Substitution Products	1257
Methods of Synthesis, 1257 - properties, 1260 - (i) Pyrimidine, Alkyl-	

and Aryl-Pyrimidines, 1261 – (ii) Halogenopyrimidines, 1262 – (iii) Nitroso- and Nitro-Pyrimidines, 1264 – (iv) Aminopyrimidines, 1265 [Monoaminopyrimidines, 1265 – Di- and Poly-aminopyrimidines, 1269] – (v) Hydroxypyrimidines, 1271 [Monohydroxypyrimidines, 1271 – Dihydroxypyrimidines, 1273 – Hydrogenated Dihydroxypyrimidines, 1276 – Trihydroxypyrimidines, 1276 – Reactions of Barbituric Acid, 1278 – Tetrahydroxypyrimidines, 1280] – (vi) Mercapto- and Alkylthio-Pyrimidines, 1281 – (vii) Aminohydroxypyrimidines, 1283 [Monoamino-monohydroxypyrimidines, 1283 – Diaminomonohydroxypyrimidines, 1285 – Monoaminodihydroxypyrimidines, 1286 – Diaminodihydroxypyrimidine, 1288 – Monoaminohydroxypyrimidines, 1290 – Triaminomonohydroxypyrimidines, 1291] – (viii) Pyrimidine Aldehydes, 1292 – (ix) Pyrimidinecarboxylic Acids, 1292	
b. Hydrogenated Pyrimidines	1295
Alloxan and Related Compounds, 1295	
c. Quinazolines (Benzopyrimidines)	1299
Methods of Synthesis, 1299 – Properties and Reactions, 1301 – (i) Quinazoline and Homologues, 1305 – (ii) Chloroquinazolines, 1305 – (iii) Aminoquinazolines, 1306 – (iv) Hydroxyquinazolines (Quinazolones) and Mercaptoquinazolines, 1307 – (v) Aldehydes and Ketones, 1311 – (vi) Carboxylic Acids, 1311 – (vii) Benzoquinazolines and Related Compounds, 1312	
d. Hydrogenated Quinazolines	1315
3. The Pyrazine Group	1318
a. Pyrazines, 1:4-Diazines	1318
Methods of Synthesis, 1319 – (i) Pyrazine, Alkyl- and Aryl-Pyrazines, 1320 – (ii) Halogenopyrazines, 1322 – (iii) Aminopyrazines, 1323 – (iv) Hydroxypyrazines, 1325 – (v) Pyrazinecarboxylic Acids, 1329 [Amino- and Hydroxy-pyrazinecarboxylic Acids, 1332]	
b. Hydropyrazines	1333
(i) Dihydropyrazines, 1333 – (ii) Tetrahydropyrazines, 1336 – (iii) Piperazines (Hexahydropyrazines), 1338 [Methods of Synthesis, 1338 – Stereochemistry of NN'-Disubstituted Piperazines, 1341 – Piperazines with Substituents on Carbon, 1342 – Ketopiperazines (Oxopiperazines), 1343]	
c. Quinoxalines (Benzopyrazines)	1345
Methods of Synthesis, 1345 – (i) Quinoxaline and its Alkyl and Aryl Derivatives, 1347 – (ii) Halogenated Quinoxalines, 1351 – (iii) Nitroquinoxalines, 1353 – (iv) Aminoquinoxalines, 1353 – (v) Hydroxyquinoxalines, 1355 [2-Hydroxyquinoxalines, 1355 – 2:3-Dihydroxyquinoxalines, 1358 – Bz-Hydroxyquinoxalines, 1360] – (vi) Quinoxaline-N-oxides, 1361 – (vii) 2-Polyhydroxyalkylquinoxalines, 1362 – (viii) Quinoxaline-2-aldehydes, 1364 – (ix) Quinoxaline-2-carboxylic Acids, 1365 [Quinoxaline-2:3-dicarboxylic Acids, 1367]	
d. Hydrogenated Quinoxalines	1368
(i) 1:2-Dihydroquinoxalines, 1368 – (ii) 1:2:3:4-Tetrahydroquinoxalines, 1368	
e. Phenazines (Dibenzopyrazines)	1371
General Methods of Synthesis, 1372 – (i) Phenazine and its Homologues, 1374 – (ii) Benzo- and Dibenzo-phenazines, 1376 – (iii) Halogenophenazines, 1377 – (iv) Nitrophenazines and Phenazinesulphonic Acid, 1378 – (v) Aminophenazines, 1380 – (vi) Hydroxyphenazines, 1381 [Dihydroxyphenazines, 1383] – (vii) Phenazinecarboxylic Acids, 1384	
f. Hydrogenated Phenazines	1385
(i) 5:10-Dihydrophenazines, 1385 – (ii) 1:2:3:4-Tetrahydrophenazines, 1387 – (iii) Octahydrophenazines, 1388 – (iv) Dodecahydrophenazines, 1389	
INDEX	1391