269. *Chemistry of the* Coprosma *Genus. Part IV. The Non-glycosidic Anthraquinone Compounds from* Coprosma lucida.

By Lindsay H. Briggs and G. A. Nicholls.

The bark of *Coprosma lucida* contains a large quantity of anthraquinone compounds present in the free state or as glycosides. This paper describes the non-glycosidic compounds, eight of which have been obtained by chromatographic absorption, *viz.*, anthragallol, its 2-methyl and 1 : 2-dimethyl ether, 1 : 6-dihydroxy-2-methylanthraquinone, rubiadin, 3-hydroxy-2-methylanthraquinone, a minute amount of an unidentified compound, and a new trihydroxy-2-methylanthraquinone, for which the name *lucidin* is proposed.

Coprosma lucida (Forster and Forster, *Char. Gen. Pl.*, 1776, 138; Oliver, " The Genus Coprosma," *Bernice P. Bishop Museum Bulletin* 132, 1935) is a robust shrub or slender tree, attaining a height of 5—6 m. and growing throughout New Zealand, to which it is endemic. It is one of the

species called " Karamu " by the Maoris, who used it for dyeing their phormium cloths shades of yellow. Aston (*New Zealand J. Sci. Tech.*, 1918, **1**, 3,264) recorded the crimson colour given by the yellow bark with alkali and the stable dyes with chrome or alumina mordants.

Preliminary investigations on the bark indicated the presence of anthraquinone compounds both in the free state and combined as water-soluble glycosides. This paper describes the former compounds; the glycosides will be described later.

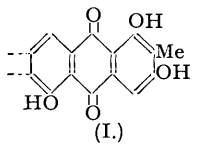
The free anthraquinone compounds could be obtained by either of two methods. In the first, the dried bark was extracted to completion with benzene, from which a compound (now named *lucidin*) separated on cooling, leaving the remaining free anthraquinone compounds in solution. The residual bark was then extracted with water to remove the glycosides, dried, and extracted to completion with acetone, from which compound *A* separated on cooling. The traces of free anthraquinone in the residual acetone solution were then combined with those extracted with benzene.

In the second method, the dried bark was extracted with acetone. Most of the free anthraquinones remained in solution but the glycosides, lucidin, and traces of the free compounds separated out on cooling. The glycosides were separated by solution in water, and the residual water-insoluble compounds added to the main quantity of the free anthraquinone compounds.

The material from both methods was taken up in dry acetone, chromatographed on calcined magnesia, and eluted with acetone until the eluate was colourless. The eluate was concentrated, and chromatographed on a fresh column. This process was repeated until all the material was adsorbed in a series of columns equivalent to one long fully developed column. The material recovered from the individual bands was rechromatographed on smaller columns, and the process repeated, on still smaller columns if necessary, until a series of compounds was obtained each giving a single band on the chromatogram.

Lucidin does not appear on the chromatogram. Its outstanding characteristic is its relative insolubility in nearly all normal organic solvents, but it could be purified by crystallisation from dioxan. Its composition, $C_{15}H_{10}O_5$, its properties, and those of its derivatives indicated a new compound. It has also been isolated from *C. acerosa* (succeeding paper).

Lucidin has colour reactions typical of a hydroxyanthraquinone, its solubility in sodium carbonate solution and positive colour reaction with ferric chloride solution indicating, respectively, at least one free β- and α-hydroxyl group. It forms a *triacetate*, a *tribenzoate*, and a *trimethyl ether* with methyl sulphate and potassium carbonate, indicating three phenolic groups. The preparation of a *monomethyl ether*, which is insoluble in sodium carbonate solution and may be characterised as its *diacetate*, indicates the presence of one β- and two α-hydroxyl groups, the former being much more readily methylated (cf. Perkin, *J.*, 1899, **75**, 433). A *C*-methyl determination, made difficult through the insolubility of lucidin in the oxidising mixture, indicates the presence of one such group, present in the β-position as shown by the isolation of 2-methylanthraquinone on distillation of lucidin with zinc. The lack of dyeing properties (on wool mordanted with dichromate or chromium, ferrous or copper sulphate) indicates that the β-hydroxy-group is not adjacent to either of the α-hydroxy-groups, and the lack of fluorescence of a glacial acetic acid solution of lucidin shows that the α-hydroxy-groups do not have a 1 : 4-relationship (cf. Raistrick, Robinson, and Todd, *Biochem. J.*, 1934, **28**, 599). There is a strong similarity in the absorption spectra of lucidin with xanthopurpurin and especially with rubiadin, indicating a 1 : 3 : 5-trihydroxy- or, less probably on phytochemical grounds, a 1 : 3 : 8-trihydroxy-structure, since no 1 : 8-compounds have yet been isolated from members of the *Rubiaceae*. The structure (I) is suggested for lucidin, but structures with the methyl group in positions 6 or 7 are not excluded.



(I.)

The compounds separated by chromatography were then examined in turn and, with one exception, have been identified with known compounds.

The first purple band was firmly attached to the magnesia and could not be removed by elution. The second band could readily be displaced from the first band, however, by the addition of a drop or two of acetic acid to the acetone used for development, a technique for which we are indebted to Mr. B. R. Thomas. The material from the first band proved to be a mixture, which was first purified by sublimation in a high vacuum and then separated by fractional crystallisation from benzene into two compounds. One, which was sparingly soluble in benzene, was identified as anthragallol by mixed m. p., colour reactions, and the preparation of the known triacetate. This is the first record of its natural occurrence, although its methyl ethers have been isolated. Perhaps the ease of oxidation of anthragallol in alkaline media has precluded its detection in the older methods of investigation where chromatography was not used.

The other compound, more readily soluble in benzene, was isolated as a red amorphous powder, m. p. 150—155°, giving violet and deep wine-red colorations in alkali and concentrated sulphuric acid respectively. Owing to the small amount of material isolated (17 mg.) and our inability to crystallise it, a detailed examination could not be made.

From the second reddish-brown band another compound was isolated; this was identified with anthragallol 2-methyl ether (Kubota and Perkin, *J.*, 1925, **127**, 1894) by its composition, m. p., and the preparation of the known diacetate and anthragallol trimethyl ether, the m. p. of the latter being undepressed by an authentic specimen. This is the first record of its natural occurrence, but it has since been isolated from *C. acerosa* (succeeding paper).

From the third pink-red band, a compound was isolated which, in our opinion, is identical with 1 : 6-dihydroxy-2-methylanthraquinone. Only 14 mg. were isolated and the compound was difficult to purify. Despite low m. p.s, 233—234° and 203—205°, compared with 289° and 215° of the known compound and its diacetate respectively, the mixed m. p. of the acetates was 210—213°, and the colour reactions, the colour of its band and its position on the chromatogram between anthragallol 2-methyl ether and anthragallol 1 : 2-dimethyl ether in both *C. lucida* (see below) and *C. acerosa* (succeeding paper), leave little doubt, in our opinion, as to its identity. Mitter (*J. Indian Chem. Soc.*, 1928, **5**, 769) considers that 1 : 6-dihydroxy-2-methylanthraquinone is identical with a compound, m. p. 282°, occurring in *Morinda umbellata* (Perkin and Hummel, *J.*, 1894, **65**, 854) and with soranjidiol, m. p. 276°, from *M. citrifolia* (Oesterle and Tisza, *Arch. Pharm.*, 1908, **246**, 158). It has been synthesised by Simonsen and Rau (*J.*, 1921, **119**, 1339) and by Bhattacharya and Simonsen (*J. Indian Inst. Sci.*, 1927, **10**, *A*, 6).

From the fourth orange band a compound has been isolated and identified with anthragallol 1 : 2-dimethyl ether by its m. p., colour reactions, and the preparation of the known acetate and of anthragallol trimethyl ether. Anthragallol 1 : 2-dimethyl ether has been isolated from the root-bark of *Oldenlandia umbellata* or chay root (Perkin and Hummel, *J.*, 1893, **63**, 1157; 1895, **67**, 817) and from *C. acerosa* (succeeding paper). It has been synthesised by Perkin and Story (*J.*, 1929, 1399).

From the fifth red band has been isolated rubiadin, identified by mixed m. p., colour reactions, and the preparation and identification of the known diacetate and dimethyl ether. This is the first recorded natural occurrence of rubiadin, but it has since been found as a trace impurity in rubiadin 1-methyl ether isolated from either *C. australis* or *C. areolata* (future communication). Its 3-glucoside, however, occurs in the root bark of *Rubra tinctorium L.* (madder) (Schunck and Marchlewski, *J.*, 1893, **63**, 969; Schunck, *Phil. Trans.*, 1853, **143**, 67), and its 3-primveroside in the root of *Galium verum* (Hill and Richter, *J.*, 1936, 1714) and *G. mollugo* (*idem*, *Proc. Roy. Soc.*, 1936—1937, **121**, *B*, 547). Rubiadin has been synthesised by Mitter and Biswas (*J. Indian Chem. Soc.*, 1930, **7**, 839), by Jones and Robertson (*J.*, 1930, 1699), and by Kusaka (*J. Pharm. Soc. Japan*, 1935, **55**, 110).

The last pink band afforded 3-hydroxy-2-methylanthraquinone, identified by m. p., colour reactions, the m. p. and composition of its acetate, and the preparation of its methyl ether. This is the first record of this compound in Nature but it has been synthesised by Baeyer and Fraude (*Annalen*, 1880, **202**, 163) and by more recent workers, including Waldmann and Sellner (*J. pr. Chem.*, 1938, **150**, 147) who record the highest m. p., 302°, compared with 260—262° of Baeyer and Fraude. Both this compound and its acetyl derivative were identical (mixed m. p.s) with specimens kindly supplied by Professor Mitter.

Experimental.

The bark was collected in December and January from Titirangi and Muriwai. The fresh bark is canary-yellow in colour, *ca.* ½ inch thick, gives a bright red colour with alkali and a green solution containing a greenish-black precipitate when warmed with dilute hydrochloric acid, the latter reaction indicative of asperuloside (forthcoming communication). The air-dried, mechanically ground bark was finally dried in a desiccator for 7—10 days.

The dried bark (162 g.) was continuously extracted with benzene (45 hours) in a Soxhlet apparatus. The same bark was dried, transferred to boiling water (800 c.c.), boiled for 20 minutes, filtered off, and washed with boiling water (200 c.c.). The aqueous extract contains the glycosides to be described in a later communication. The bark was again dried and extracted to completion with acetone (15 hours; Soxhlet). Yellow needles separated from the hot acetone extract and a further crop separated on concentration. This *lucidin* (2·2 g.) was filtered off, and the extract concentrated to *ca.* 30 c.c. and poured into water. The yellow precipitate (450 mg.) gave the same chromatogram in a test as the material from the benzene extract, to which it was then added.

The whole of the material from the benzene extract (6·2 g.), including the small amount from the acetone extract, was heated under reflux with alcohol (250 c.c.) and filtered hot. A yellow pigment was filtered off (220 mg.) which proved to be identical with lucidin from the acetone extract. On cooling and standing, the alcoholic solution deposited brown amorphous material (800 mg.) which gave no

colour with alkali and was neglected. The remaining alcoholic solution was taken to dryness, and the residue dissolved in dry acetone and chromatographed on fresh or calcined magnesia (B.P. magnesia levis), sieved before use. Alumina could not be used as even from poor grades the colouring matters could not be removed after absorption.

Lucidin.—This was purified by solution in 2% sodium hydroxide solution, filtering and reprecipitating by acidification. After repeated crystallisation from dioxan, it formed yellow needles, m. p. above 330°, giving a single band when chromatographed on magnesia from a dioxan solution (Found : C, 66·4; H, 3·9. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%). The *C*-Me value, as determined by the Kuhn–Roth method, was difficult to obtain owing to the insolubility of the material in the oxidising medium (Found : *C*-Me, 4·7. $C_{15}H_{10}O_5$ requires *C*-Me, 10·0%). A Zeisel determination likewise could not be made owing to the insoluble nature of lucidin, but other facts indicate the absence of methoxy-groups.

Absorption Spectra.—The absorption spectra of the following compounds were measured in concentrated sulphuric acid and alcoholic solution using a Beckmann model DU spectrophotometer. We are greatly indebted to Mr. T. J. Sprott for these measurements.

In H_2SO_4.		In EtOH.		In H_2SO_4.		In EtOH.		In H_2SO_4.		In EtOH.	
log ε.	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.
Lucidin.				1 : 3-Dihydroxyanthraquinone.				Rubiadin.			
4·18	2460 *	4·47	2460	3·90	2650	4·43	2460	4·12	2460	4·39	2460
4·35	2890	4·46	2800	3·99	2870	4·36	2840	4·48	2890	4·52	2800
3·97	3200 *	—	—	3·71	3200	—	—	3·96	3200 *	—	—
4·07	4600	3·88	4150	3·73	4600	3·79	4150	4·02	4600	3·87	4150

* Points of inflexion.

Lucidin is soluble in 10% sodium hydroxide, sodium carbonate, and ammonium hydroxide solutions, giving red solutions, soluble in concentrated sulphuric acid with an orange-red colour, and gives a brown coloration with ferric chloride solution.

Triacetate. Lucidin (100 mg.) was heated with acetic anhydride (1·5 c.c.) and pyridine (2 c.c.) for ½ hour. After the mixture had been poured on cracked ice (100 g.), the *triacetate* (135 mg.) crystallised from alcohol in pale yellow needles of constant m. p. 175—178° (Found : C, 63·8; H, 4·6. $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·2%).

Tribenzoate. Lucidin (100 mg.) was heated with benzoyl chloride (1 c.c.) and pyridine (4 c.c.) for an hour and transferred to ice-cold water (150 c.c.). After standing, the solution was decanted from the oily red mass which separated, and the latter was triturated with 5% sodium hydrogen carbonate solution (100 c.c.), filtered off, and washed with the minimum of alcohol. The almost colourless *tribenzoate* then crystallised from glacial acetic acid in pale yellow prisms of constant m. p. 204—205° (Found : C, 72·7; H, 4·2. $C_{36}H_{22}O_8,H_2O$ requires C, 72·0; H, 4·0%).

Monomethyl ether. A solution of lucidin (1 g.) in acetone (75 c.c.) was heated with methyl sulphate (3 c.c.) and anhydrous potassium carbonate (10 g.) for ½ hour. The carbonate was filtered off, washed with acetone, shaken, and washed with water until the filtrate was colourless. The red insoluble potassium salt afforded the *monomethyl ether* on treatment with dilute hydrochloric acid, crystallising from alcohol in orange-yellow needles of constant m. p. 184·5—185° (Found : C, 66·0; H, 4·5; OMe, 10·8. $C_{16}H_{12}O_5,\frac{1}{2}H_2O$ requires C, 65·5; H, 4·5; OMe, 10·6%). The monomethyl ether forms a red insoiuble sodium salt with sodium hydroxide solution but is insoluble without change of colour in sodium carbonate solution. Ferric chloride gives a brown coloration. The *diacetate* was formed from the monomethyl ether (150 mg.) by acetylation with acetic anhydride (1 c.c.) and concentrated sulphuric acid (1 drop). The product (180 mg.) from pouring the mixture into ice-cold water (50 c.c.), after repeated crystallisation from acetic anhydride, formed yellow plates, m. p. 173—174·5° (Found : C, 64·9; H, 4·2; Ac, 23·1. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4; 2Ac, 23·4%).

Trimethyl ether. The acetone filtrate and acetone washings from the preparation of the monomethyl ether were concentrated to a small volume and poured into water. The pale yellow precipitate (300 mg.) gave no colour change with alkali and crystallised from alcohol in pale yellow needles of constant m. p. 173° (Found : C, 68·2, H, 5·05; OMe, 22·1, 22·5. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·2; 3OMe, 29·8%). By increasing the reaction time in the above preparation to 24 hours, lucidin could be completely converted into the fully methylated derivative.

Distillation of Lucidin with Zinc Dust.—A mixture of lucidin (200 mg.) and zinc dust (4 g.) was heated in a hard-glass tube in a stream of hydrogen, with a further quantity of zinc dust (1 g.) beyond the mixture. The pure zinc dust was kept at a dull red heat while the mixture was gradually raised to the same temperature. The sublimate (10 mg.) from the cool part of the tube, together with that from a second distillation, crystallised from alcohol in almost colourless leaflets, and after three crystallisations had m. p. 202°, and 211—213° when mixed with pure 2-methylanthracene, m. p. 216°, kindly presented by Dr. B. Siegfried, Zofingen.

Chromatographic Separation of the Remaining Colouring Matters.—The whole solution of the remaining free anthraquinone compounds in acetone was poured over one absorption column (5 × 12 cm.) and eluted until the eluate was almost colourless. The eluate was concentrated to 120—150 c.c., and the process repeated on fresh columns until all the coloured compounds were absorbed and developed in a series of columns.

The final colourless eluate, on concentration to *ca.* 5 c.c., deposited colourless needles (30 mg.) which, after recrystallisation from acetone, had m. p. 210—220°. The compound did not dissolve in 10% sodium hydroxide solution or in concentrated sulphuric acid and was not further examined.

In the case of the first section of the series this alone was further eluted with acetone containing sufficient glacial acetic acid (2 c.c.) for the removal of the second band from the first, which remained unchanged. The columns were then extruded, cut into their bands, and decomposed with dilute hydrochloric acid. The material from the second, fourth, and fifth larger bands was purified by dissolving

in acetone and rechromatographing. The material from the smaller bands, together with that from the corresponding bands of the rechromatographs, was rechromatographed on 2·7-cm. diameter columns. The material from the final small bands was collected and chromatographed on 1·7-cm. diameter tubes, a system which separated all the components into pure chromatograms.

Identification of the Compounds from the Chromatograph Bands.

Band I (147 mg.) : *Anthragallol, and an Unidentified Compound.*—The amorphous brown substance from this band was first sublimed at 110—180°/0·01 mm. The red sublimate (38 mg.) was separated into two fractions by their difference of solubility in benzene. The orange-brown, sparingly soluble portion (14 mg.) crystallised from nitrobenzene in needles, m. p. 310° undepressed by a specimen of anthragallol. This dissolved in 10% sodium hydroxide solution with a green colour, oxidising in air to a brown solution, a reaction typical of anthragallol. The acetate crystallised from glacial acetic acid as pale yellow needles, m. p. 187—189°, undepressed by anthragallol triacetate.

From the benzene-soluble fraction was obtained a bright red substance (17 mg.), m. p. 150—155°, insoluble in water but readily soluble in organic solvents. This could not be purified and has not been identified.

Band II (1·6 g.) : *Anthragallol 2-Methyl Ether.*—From this band an amorphous brown substance was isolated which sublimed as yellow needles below 180° and melted at 215—218°. It could not be conveniently recrystallised, so was repurified by sublimation at 160—180°/0·01 mm. and then had m. p. 218° (Found : C, 66·5; H, 3·9; OMe, 9·9. Calc. for $C_{15}H_{10}O_5$: C, 66·7; H, 3·7; OMe, 11·5%). It gave a red colour with alkali and concentrated sulphuric acid. Kubota and Perkin (*loc. cit.*) record yellow needles, m. p. 218—220°, for anthragallol 2-methyl ether with the same colour reactions. In addition, the compound is soluble in 5% sodium carbonate solution and gives a brown coloration with ferric chloride solution. The acetate, prepared by acetylation with acetic anhydride and concentrated sulphuric acid, crystallised from alcohol in long yellow rods, m. p. 145—146·5°, unchanged by further crystallisation. Kubota and Perkin (*loc. cit.*) describe their acetate as large prismatic needles, m. p. 152—154°.

Anthragallol trimethyl ether was prepared from the monomethyl ether (60 mg.) with methyl sulphate and anhydrous potassium carbonate in acetone solution. After crystallisation from acetone it had m. p. 167°, undepressed by an authentic specimen (Bock, *Monatsh.*, 1902, **23**, 100).

Band III (14 mg.) : 1 : 6-*Dihydroxy-2-methylanthraquinone.*—The small quantity of pigment from this band could not be readily purified. After two attempts to crystallise it from 60% ethyl alcohol it softened on heating to 220° and commenced to sublime as yellow needles before melting at 233—234°. Its colour reactions, red with 10% sodium hydroxide solution, brown-red with concentrated sulphuric acid, brown with ferric chloride solution, and its solubility in sodium carbonate solution are the same as those of 1 : 6-dihydroxy-2-methylanthraquinone, m. p. 290°, isolated from a similar band on the chromatogram of the pigments from *C. acerosa* (succeeding paper). Simonsen and Rau (*loc. cit.*) describe this compound as brown needles, m. p. 281°, giving a red colour in alkali and sulphuric acid.

The compound (8 mg.) was acetylated by warming with acetic anhydride (0·5 c.c.) and concentrated sulphuric acid (1 drop) to 60—70° for 10 minutes. The product (6 mg.), formed by pouring the mixture into water, crystallised from alcohol in pale yellow needles, m. p. 203—205°, raised to 210—213° on admixture with the diacetate of 1 : 6-dihydroxy-2-methylanthraquinone, m. p. 214°, which Simonsen and Rau (*loc. cit.*) describe as yellow needles, m. p. 212°.

Band IV (87 mg.) : *Anthragallol* 1 : 2-*Dimethyl Ether.*—The yellow pigment from this band crystallised from alcohol in rhombohedral plates of constant m. p. 233—236°. It gives an orange-red solution with alkali, is insoluble in sodium carbonate solution, and gives no colour reaction with ferric chloride solution. Perkin and Story (*loc. cit.*) describe anthragallol 1 : 2-dimethyl ether as yellow plates, m. p. 230—232°, giving a red colour with alkali. The acetate, prepared as for the previous derivative, crystallised from alcohol in long yellow needles, m. p. 177—179°. Perkin and Story describe the acetate of anthragallol 1 : 2-dimethyl ether as bright yellow needles, m. p. 177—179°. The product from methylation, carried out as before, crystallised from acetone in pale yellow needles, m. p. 169°, undepressed by a sample of anthragallol trimethyl ether.

Band V (160 mg.) : *Rubiadin.*—The yellow pigment from this band crystallised from glacial acetic acid in yellow plates, m. p. 302°, undepressed by an authentic specimen of rubiadin of the same m. p. Schunck and Marchlewski (*J.*, 1893, **63**, 969; 1894, **65**, 182) and later workers record m. p. 290° for rubiadin. The acetate crystallised from acetic anhydride in lemon-yellow rods, m. p. 228°, undepressed by an authentic specimen of rubiadin diacetate, m. p. 230°. Schunck and Marchlewski (*loc. cit.*), Simonsen (*J.*, 1920, **117**, 561), and Mitter and Gupta (*J. Indian Chem. Soc.*, 1928, **5**, 25) all record m. p. 225° for this derivative. Methylation as in the previous cases afforded rubiadin dimethyl ether, crystallising from alcohol in lemon-yellow needles, m. p. 160·5°, undepressed by an authentic specimen (Briggs and Dacre, *J.*, 1948, 564).

The rubiadin required for comparison purposes was obtained by demethylation of its 1-methyl ether (*ex C. australis*) (240 mg.) by heating with concentrated sulphuric acid (4 c.c.) at 150° for 10 minutes. The olive-green precipitate (160 mg.), formed on pouring the mixture into water, crystallised from 60% dioxan–water (charcoal) in golden-yellow rods, or from glacial acetic acid as plates of constant m. p. 302°.

Band VI (66 mg.) : 3-*Hydroxy-2-methylanthraquinone.*—The compound from this band crystallised from glacial acetic acid in yellow needles which sublimed before melting at 302°, the m. p. recorded by Waldmann and Sellner (*loc. cit.*) for 3-hydroxy-2-methylanthraquinone. This compound (20 mg.) was acetylated as for the other cases described above. After crystallisation from alcohol, 3-acetoxy-2-methylanthraquinone formed long, flat, yellow needles, m. p. 184° (Found : C, 72·5; H, 5·0. Calc. for $C_{17}H_{12}O_4$: C, 72·85; H, 4·3%). Bistrzycki and Zen-Ruffinen (*Helv. Chim. Acta*, 1920, **3**, 378) give m. p. 176°. The original compound and the acetyl derivative were identical (mixed m. p.) with authentic samples supplied by Prof. Mitter.

The original compound (6 mg.) was methylated as described previously. The precipitated product (4·5 mg.), after two crystallisations from alcohol, had m. p. 196°. Waldmann and Sellner (*loc. cit.*) record m. p. 197° for 3-methoxy-2-methylanthraquinone.

The analyses are by Drs. Weiler and Strauss, Oxford, and Mr. R. N. Seelye of this College.

We are indebted to the Chemical Society, the Royal Society of New Zealand, the Australian and New Zealand Association for the Advancement of Science, and the Research Fund Committee of the University of New Zealand for grants, and to Imperial Chemical Industries for gifts of chemicals, and one of us (G. A. N.) to the University of New Zealand for a Duffus Lubecki Scholarship and a Research Fund Fellowship.

AUCKLAND UNIVERSITY COLLEGE,
AUCKLAND, NEW ZEALAND.

[*Received, November 24th*, 1948.]