Chemistry of the *Coprosma* Genus. Part XIV.[1] Constituents of Five New Zealand Species

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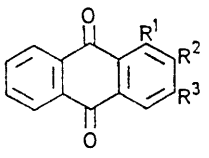
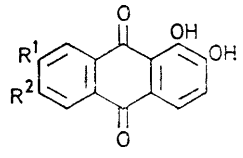
The anthraquinone pigments of the barks of *Coprosma tenuicaulis, C. linariifolia, C. rotundifolia,* and *C. propinqua* and the heartwood of *C. robusta* are reported. *C. linariifolia* contains a new anthragallol 2-methyl ether 3-glycoside and *C. rotundifolia* a rubiadin 3-glycoside. A minor anthraquinone of *C. lucida* previously considered to be soranjidiol has been identified as lucidin. The presence of the coumarin scopoletin has been shown in the barks of a number of *Coprosma* species.

THE genus *Coprosma* (family Rubiaceae) is well developed in New Zealand where it is noted for the occurrence of anthraquinone pigments in the barks of many species. In a continuation of our systematic study of the genus we report results from the examination of five New Zealand species for the presence of anthraquinones. In each case compounds were isolated by multiple chromatography of acetone or alcoholic extracts on columns of magnesium carbonate or magnesium oxide.

The bark of *Coprosma tenuicaulis* Hook.f.,[2a] † a shrub up to *ca.* 3 m high which is found mainly in the North Island, contained a high proportion (4.1%) of rubiadin 1-methyl ether (1).[4] Minor constituents included rubiadin (2),[4] 3-hydroxy-2-methylanthraquinone (3),[5] and a further pigment which was identified as 1,2-dihydroxy-6(or 7)-methylanthraquinone [(10) or (11)]. Although a 6-methylalizarin structure is favoured,[6] the ambiguity of syntheses [7] of each isomer do not allow complete identification of our compound. Also isolated were sucrose and scopoletin (12), the first coumarin to be found in a *Coprosma* species.

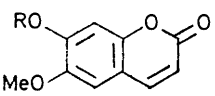
C. linariifolia Hook.f.[2b] is a small tree up to 6 m high with a bark of considerable tinctorial power. Extraction of the bark gave a new water-soluble anthraquinone glycoside which was isolated directly from a glycoside mixture as an ethanol solvate, $C_{26}H_{28}O_{14}$,EtOH. Hydrolysis gave anthragallol 2-methyl ether (4) [8] and equal amounts of glucose and xylose. Since the quinonoid carbonyl bands were in similar positions to those of anthragallol 2-methyl ether,[9] the sugar residues are assigned to C-3 where they probably occur as the common primeverose unit. The remaining anthraquinones were also present as water-soluble glycosides and the mixture was hydrolysed and the aglycones were chromatographed on magnesium oxide. Compounds identified by mass spectrometry of bands obtained from the column were anthragallol 2-methyl ether (4),‡ rubiadin 1-methyl ether (1), rubiadin (2), 3-hydroxy-2-methylanthraquinone (3), and nordamnacanthal (5).[10]





(1) R^1 = OMe, R^2 = Me, R^3 = OH
(2) R^1 = OH, R^2 = Me, R^3 = OH
(3) R^1 = H, R^2 = Me, R^3 = OH
(4) R^1 = R^3 = OH, R^2 = OMe
(5) R^1 = R^3 = OH, R^2 = CH:O
(6) R^1 = OMe, R^2 = CH_2OH, R^3 = OH
(7) R^1 = R^3 = OH, R^2 = CH_2OH
(8) R^1 = OH, R^2 = Me, R^3 = glucosyl
(9) R^1 = OH, R^2 = Me, R^3 = H

(10) R^1 = H, R^2 = Me
(11) R^1 = Me, R^2 = H



(12) R = H
(13) R = glucosyl

The bark of the lowland forest shrub *C. rotundifolia* A. Cunn.[2c] afforded rubiadin 1-methyl ether (1), rubiadin (2), damnacanthol (6),[10] lucidin (7),[8] scopoletin (12), scopolin (13),[11] glucose, and unidentified anthraquinone glycosides. One of the latter was obtained as golden prisms, m.p. 209.5—210.5°, analysis of which corresponded to a hemihydrate, $C_{26}H_{28}O_{13}$,$0.5H_2O$. Colour reactions and the i.r. spectrum showed that the compound

† In ref. 3 this species is mistakenly referred to as *C. parviflora*
‡ The suspected anthragallol 1,3-dimethyl ether reported from this source [3] has been shown to be impure anthragallol 2-methyl ether.

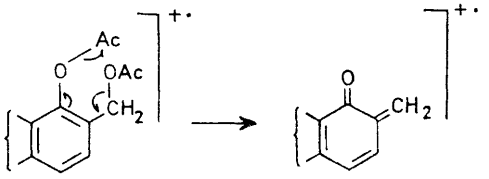
[1] Part XIII, L. H. Briggs, B. F. Cain, P. W. Le Quesne, and J. N. Shoolery, *J. Chem. Soc.*, 1965, 2595.
[2] H. H. Allan, 'Flora of New Zealand,' Government Printer, Wellington, 1961, vol. 1 (*a*) p. 578, (*b*) p. 569, (*c*) p. 577, (*d*) p. 572, (*e*) p. 582.
[3] L. H. Briggs, in 'Chemistry of Natural and Synthetic Colouring Matters and Related Fields,' eds. T. S. Gore, B. S. Joshi, S. V. Sunthankar, and B. D. Tilak, Academic Press, New York, 1962, p. 137.
[4] L. H. Briggs and J. C. Dacre, *J. Chem. Soc.*, 1948, 564; L. H. Briggs, G. A. Nicholls, and R. M. L. Patterson, *ibid.*, 1952, 1718.
[5] L. H. Briggs and B. R. Thomas, *J. Chem. Soc.*, 1949, 1246.
[6] E. J. C. Brew and R. H. Thomson, *J. Chem. Soc.* (*C*), 1971, 2001.
[7] (*a*) St. von Niemientowski, *Ber.*, 1900, **33**, 1629; (*b*) F. Mayer and H. Gunther, *Ber.*, 1930, **63**, 1455; (*c*) P. C. Mitter and H. G. Biswas, *J. Indian Chem. Soc.*, 1928, **5**, 769; (*d*) P. C. Mitter and A. K. Sarkar, *ibid.*, 1930, **7**, 619.
[8] L. H. Briggs and G. A. Nicholls, *J. Chem. Soc.*, (*a*) 1949, 1241; (*b*) 1953, 3068.
[9] H. Bloom, L. H. Briggs, and B. Cleverley, *J. Chem. Soc.*, 1959, 178.
[10] J. H. Bowie and R. G. Cooke, *Austral. J. Chem.*, 1962, **15**, 332; J. H. Bowie, R. G. Cooke, and P. E. Wilkin, *ibid.*, p. 336.
[11] W. Grassmann, H. Endres, W. Pauckner, and H. Mathes, *Chem. Ber.*, 1957, **90**, 1125.

was an anthraquinone glycoside which possessed at least one phenolic group (3 380 cm^{-1}). The spectrum also showed both bonded and non-bonded carbonyl groups (1 625 and 1 660 cm^{-1}) and four adjacent aryl protons (712 cm^{-1}) indicating that the phenolic group was in an α-position and that all substituents were on one aryl ring. Treatment of the glycoside with dilute hydrochloric acid effected only partial hydrolysis giving rubiadin 3-glucoside (8). Xylose and a trace of glucose were present in the hydrolysate. Although the possibility of a 3α-primeveroside cannot be discounted, it appears that our compound is identical with the rubiadin 3β-primeveroside (m.p. 248—250°) found in *Galium* species.[12] The low m.p. of our sample may be due to solvate formation.

C. propinqua A. Cunn.[2d] is a bushy shrub, 3—6 m tall which is found in lowland areas of New Zealand. The bark gave scopoletin (12), glucose, rhamnose, and a high yield of asperuloside,[1] but only traces of anthraquinones.

Although the bark of *C. robusta* Raoul [2e] is devoid of colouring matter, the heartwood of this shrub gave rubiadin 1-methyl ether (1), rubiadin (2), scopoletin (12), glucose, asperuloside, and, as minor components, unidentified anthraquinones.

In Part IV [8] we reported the isolation from *C. lucida* J. R. et G. Forst. of a minor anthraquinone which, despite its low m.p. and that of its acetate, was tentatively identified as soranjidiol (9). Reinvestigation has now shown that this compound is lucidin (7). Repeated recrystallization of the sample until it was homogeneous by t.l.c. (light petroleum–acetone 3 : 1), raised the m.p. to >300°, giving a sample with u.v. and i.r. spectra identical with those of authentic lucidin. The derived acetate and dimethyl ether were also identical with authentic samples. The mass spectrum of lucidin triacetate was of interest since, in addition to peaks and metastable ion peaks corresponding to the loss of three acetate groups as keten (*m/e* 354, 312, and 270), a more intense metastable ion peak due to the loss of 102 mass units from the molecular ion was present. This corresponds to, and appears to be diagnostic of, the fragmentation (14) ⟶ (15).



(14) (15)

A comprehensive examination of methods for the rapid separation and identification of anthraquinone pigments was also undertaken. In general, paper chromatography,[13,14] column chromatography, and thin-layer electrophoresis [14] were unsatisfactory. T.l.c. and p.l.c. [light petroleum–acetone (3 : 1) and butanol–acetic acid–water (12 : 3 : 5) on Keiselgel DG] appeared to give the best separation except for polyhydroxylated anthraquinones. Magnesium silicate was a satisfactory adsorbent for glycosides and polyhydroxyanthraquinones and cellulose–silica gel [15] for glycosides, but polyamide plates [16] were too fragile for spraying.

In view of the detection of scopoletin (12) in *C. tenuicaulis*, *C. rotundifolia*, *C. propinqua*, and *C. robusta*, a search for this compound in other species was carried out. Co-chromatography of bark extracts indicated its presence in *C. arborea* Kirk, *C. areolata* Cheesem., and *C. rubra* Petrie, but absence in *C. acerosa* A. Cunn., *C. australis* (A. Rich.) Robinson, *C. foetidissima* J. R. et G. Forst., *C. linariifolia* Hook.f., *C. lucida* J. R. et G. Forst., *C. parviflora* Hook.f., and *C. pseudocuneata* W. R. B. Oliver. However, most species gave spots which fluoresced under u.v. light, suggesting the presence of coumarins.

EXPERIMENTAL

For general experimental details see Part XIII.[1] Unless otherwise stated column chromatography of anthraquinones was carried out on heavy magnesium carbonate. In general, columns were fully developed with acetone and faster moving bands were collected by elution. Slower moving bands were recovered by extrusion of the column and treatment with dilute hydrochloric acid in methanol. Final purification was frequently effected by preparative thin layer chromatography (p.l.c.) on Kieselgel DG (Riedel–de Haen). Solvent systems for paper chromatography and t.l.c. were (A) butanol–pyridine–water (3 : 1 : 1), (B) ethyl acetate–acetic acid–water (3 : 1 : 3), (C) light petroleum–acetone (3 : 1), (D) benzene–ethyl acetate–acetic acid (75 : 24 : 1), (E) butanol–acetic acid–water (4 : 1 : 5), (F) aqueous 10% acetic acid, and (G) water. All compounds were identified by comparison of their i.r.[17] and u.v. spectra and colour reactions with those of authentic samples, and where appropriate, by preparation of acetates and methyl ethers.

Species were identified by Dr. R. C. Cooper, formerly Botanist, Auckland Institute and Museum, or by Dr. L. B. Moore, formerly Botany Division, D.S.I.R., Canterbury.

Coprosma tenuicaulis.—The dried and ground root bark (1.2 kg), collected near Ohakune, central North Island (Auckland Institute and Museum Herbarium nos. 50072, 50947, 50948), was extracted (Soxhlet) successively with light petroleum (10 h), acetone (65 h), and methanol (60 h). The light petroleum extract gave a waxy material (0.97 g) and traces of anthraquinones and was not investigated further. Concentration of the acetone extract gave a precipitate of rubiadin 1-methyl ether (45 g, 3.7%), which afforded yellow needles, m.p. and mixed m.p. 282—284° (with sublimation from 258°) (from dioxan).

Water was added to the final acetone concentrate and the resulting precipitate (5.0 g) was column chromatographed to give (i) rubiadin 1-methyl ether (4.2 g, 0.4%); (ii) rubiadin (80 mg), bronze rods (from chloroform or acetic acid), m.p. and mixed m.p. 301°; (iii) 3-hydroxy-2-methyl-

[12] R. Hill and D. Richter, *J. Chem. Soc.*, 1936, 1714.
[13] S. Shibata, M. Takito, and A. Tanaka, *J. Amer. Chem. Soc.*, 1950, **72**, 2789.
[14] J. Franc and M. Wurst, *Coll. Czech. Chem. Comm.*, 1960, **25**, 657.
[15] N. A. Turner and R. J. Redgwell, *J. Chromatog.*, 1966, **21**, 129.
[16] R. J. T. Graham, *J. Chromatog.*, 1968, **33**, 118.
[17] R. H. Thomson, ' Naturally Occurring Quinones,' Academic Press, New York, 2nd edn., 1971.

anthraquinone (20 mg) (purified by repeated p.l.c. from light petroleum–acetone, 2 : 1) which crystallized from acetic acid as leaflets, m.p. 293—296° (with sublimation from 220°), not depressed by admixture with an authentic sample kindly provided by Dr. L. R. Row; (iv) 1,2-dihydroxy-6(or 7)-methylanthraquinone (32 mg) which crystallized from benzene as orange needles, m.p. 219° (lit.,[7d] for 1,2-dihydroxy-6-methylanthraquinone, 218—219°) (Found: C, 71.3; H, 4.3. Calc. for $C_{15}H_{10}O_4$: C, 70.9; H, 4.0%), $\lambda_{max.}$ 221.5 (log ε 4.37), 247.5 (4.43), 268 (4.39), 285 infl (4.27), and 430 nm (3.61), $\nu_{max.}$ 3 390 (β-OH), 1 672 (non-bonded conj. CO), and 1 637 cm^{-1} (bonded conj. CO); the compound gave intense blue colourations in sodium carbonate and sodium hydroxide solutions, and a transient blue changing to an intense violet colour in concentrated sulphuric acid; and (v) a polyhydroxyanthraquinone (2.5 mg), $\lambda_{max.}$ 246.5, 277.5, and 410 nm, $\nu_{max.}$ 3 415 (β-OH) and 1 675 cm^{-1} (non-bonded conj. CO).

The water soluble fraction was liquid–liquid extracted with ethyl acetate for 10 h to give scopoletin (0.18 g), which crystallized from ethanol as needles, m.p. and mixed m.p. 206—206.5°.

Paper chromatography of the remaining aqueous solution in system (A) showed the presence of glucose and rhamnose.

Concentration of the methanolic extract gave sucrose (0.75 g), which crystallized from methanol as monoclinic crystals, m.p. and mixed m.p. 179—180°, $[\alpha]_D^{25}$ +63.3° (*c* 1.0 in H_2O). T.l.c. of the extract showed the presence of the same anthraquinones as in the acetone extract.

Similar results were obtained by extraction of the aerial bark. Extraction of the heartwood with ether and ethyl acetate gave scopoletin (1%), but no anthraquinones.

C. linariifolia.—The dried and ground bark (282 g), collected from Kennedy's Bush, Southern Alps, was extracted (Soxhlet) with ethanol (14 h). Concentration of the extract gave a water-soluble precipitate of an *anthragallol 2-methyl ether 3-glycoside* (3.9 g), which crystallized from ethanol as small yellow needles, m.p. 245—247° (Found: C, 54.9; H, 5.45; OMe, 4.4. $C_{26}H_{28}O_4$,EtOH requires C, 55.1; H, 5.6; OMe, 5.1%), $\nu_{max.}$ 3 378 (OH), 1 670 (non-bonded conj. CO), and 1 634 cm^{-1} (bonded conj. CO). The compound was hydrolysed with 5% sulphuric acid under reflux for 2 h to give anthragallol 2-methyl ether, which was purified by sublimation at 140 °C and 0.04 mmHg as yellow needles, m.p. 216° (Found: C, 67.05; H, 3.85. Calc. for $C_{15}H_{10}O_5$: C, 66.7; H, 3.7%); methyl ether, m.p. and mixed m.p. 171°. Examination of the de-acidified (Amberlite IRA-400 resin) hydrolysate by paper chromatography in system (B) showed the presence of glucose and xylose.

The remaining extract was hydrolysed by heating under reflux with 5% sulphuric acid and the product (3 g) was chromatographed from acetone on magnesium oxide to give (i) anthragallol 2-methyl ether (20 mg), m.p. and mixed m.p. 216° (Found: $M^{+\cdot}$, 270.0529. Calc. for $C_{15}H_{10}O_5$: *M*, 270.0528); exchange with D_2O showed the presence of two phenolic groups; (ii) a crystalline mixture of rubiadin 1-methyl ether (Found: $M^{+\cdot}$, 268.0734. Calc. for $C_{16}H_{12}O_4$: *M*, 268.0735), rubiadin (Found: $M^{+\cdot}$ 254.0576. Calc. for $C_{15}H_{10}O_4$: *M*, 254.0579), and 3-hydroxy-2-methylanthraquinone (Found: $M^{+\cdot}$, 238.0630. Calc. for $C_{15}H_{10}O_3$: *M*, 238.0625). Two-dimensional t.l.c. in solvents (C) and (D) gave spots corresponding to those of authentic samples; and (iii) a crystalline mixture of anthragallol 2-methyl ether (Found: $M^{+\cdot}$ 270.0525. Calc. for $C_{15}H_{10}O_5$: *M*, 270.0528), rubiadin (Found: $M^{+\cdot}$, 254.0578. Calc. for $C_{15}H_{10}O_4$: *M*, 254.0579), nordamnacanthal (Found: $M^{+\cdot}$, 268.0368. Calc. for $C_{15}H_8O_5$: *M*, 268.0372); and 3-hydroxy-2-methylanthraquinone (Found: $M^{+\cdot}$, 238.0625. Calc. for $C_{15}H_{10}O_3$: *M*, 238.0630). Exchange with D_2O showed the presence of two phenolic groups in the first three compounds and one in the last.

C. rotundifolia.—The dried and ground bark (163 g), collected from the Orongorongo Valley, Wellington, was extracted (Soxhlet) successively with light petroleum (3.5 h), acetone (74 h), and methanol (63 h). The light petroleum extract gave a waxy solid (1.42 g), m.p. 84—85°, which was not investigated further, and a pigment which was column chromatographed to give rubiadin 1-methyl ether (2 mg), m.p. and mixed m.p. 289° (with sublimation from 258°).

The acetone extract was repeatedly chromatographed to give (i) rubiadin 1-methyl ether (0.27 g), m.p. and mixed m.p. 292—294° (with sublimation from 258°); (ii) rubiadin (22 mg), m.p. and mixed m.p. 300—301°; (iii) an unidentified anthraquinone (22 mg) which crystallized from ethyl acetate as orange needles, m.p. 312° (with darkening above 230°), $\nu_{max.}$ 3 390 (β-OH), 1 675 (non-bonded conj. CO), and 1 652 cm^{-1} (non-bonded conj. CO) [the compound gave a red colour with sodium carbonate and sodium hydroxide solutions, a red-brown with concentrated sulphuric acid, and a negative reaction in the iron(III) chloride test]; (iv) damnacanthol [10] (55 mg), which crystallized from acetic acid as yellow needles, m.p. >300° (with darkening above 220°), identical with an authentic sample kindly provided by Professor Y. Hirose; (v) lucidin [8] (27 mg), which crystallized from aqueous acetone as orange needles, m.p. >330° (with darkening above 240°) (Found: $M^{+\cdot}$, 270.0522. Calc. for $C_{15}H_{10}O_5$: *M*, 270.0528); acetate, m.p. and mixed m.p. 170—171°, δ 2.03 (OAc), 2.41 (OAc), 2.55 (OAc), 5.23 (s, $ArCH_2$·OAc), and 7.1—8.1 (m, ArH); dimethyl ether, m.p. and mixed m.p. 172—173° (Found: $M^{+\cdot}$, 298.0837. Calc. for $C_{17}H_{14}O_5$: *M*, 298.0841), δ 3.97 (s, OMe), 4.03 (s, OMe), and 4.84 (s, $ArCH_2$·OH); (vi) scopoletin, identified by its u.v. spectrum and by paper chromatographic comparison with an authentic sample in systems (E)—(G); (vii) scopolin, which had R_F values identical with those recorded [18] for systems (E) and (G) and the same colour under u.v. both before and after exposure to ammonia vapour; $\lambda_{max.}$ 217 (rel. log *D* [19] 13.6), 291 (7.6), and 338 nm (7.9); and (viii) unidentified anthraquinones.

The later fractions were rechromatographed from aqueous methanol on a polycaprolactam [11,20] column to give *rubiadin 3-glycoside* (151 mg), which crystallized from methanol–acetic acid as long golden prisms, m.p. 209.5—210.5° (Found: C, 55.9; H, 5.9. $C_{26}H_{28}O_{13}$,$0.5H_2O$ requires C, 56.0; H, 5.2%), $\lambda_{max.}$ 242 (rel. log *D* 9.54), 265 (11.49), 277 (11.73), and 344 (9.11), $\nu_{max.}$ 3 380 (β-OH), 2 900, 1 660 (non-bonded conj. CO), 1 625 (bonded conj. CO), 1 590, 1 287, 858, and 712 cm^{-1} (4 adj. ArH).

The glycoside was heated under reflux with 10% hydrochloric acid for 8 h to give rubiadin 3-glucoside, which crystallized from aqueous ethanol as yellow needles, m.p. 242—243° (Found: C, 59.4; H, 5.3. Calc. for $C_{21}H_{20}O_9$,-$0.5H_2O$: C, 59.3; H, 5.0%), $\lambda_{max.}$ 238 (rel. log *D* 15.8), 281 (11.7), and 337 nm (8.6), $\nu_{max.}$ 3 380 (β-OH), 2 920, 2 860, 1 665 (non-bonded conj. CO), 1 630 (bonded conj. CO), 1 593, 1 287, 1 118, 1 072, 777, 744, and 711 cm^{-1} (4 adj. ArH).

[18] J. B. Harborne, *Biochem. J.*, 1960, **74**, 270.
[19] A. E. Bradfield and A. E. Flood, *J. Chem. Soc.*, 1952, 4740.
[20] W. Grassmann, H. Hörmann, and A. Hartle, *Macromol. Chem.*, 1956, **21**, 37.

The presence of glucose and an unidentified sugar (R_{Glc} 0.55) in the methanolic extract was shown by paper chromatography in system (E).

Extracts from a further sample of bark collected at Te Whaiti, Urewera, gave similar results.

C. propinqua.—The dried and ground bark (750 g), collected from Erua, Tongariro National Park, North Island, was extracted (Soxhlet) successively with light petroleum (9 h), acetone (26 h), and methanol (26 h). The light petroleum extract gave a small amount of an oil and a waxy solid, m.p. 79—80°, which were not investigated further. The acetone extract gave asperuloside [1] (35.2 g, 4.7%), m.p. and mixed m.p. 129—131°, and a tar which was extracted under reflux with ether. The extract contained scopoletin, identified as above. Acetylation of the ether-insoluble residue gave asperuloside tetra-acetate (17.4 g), m.p. and mixed m.p. 152—154°.

The presence of glucose and rhamnose in the methanolic extract was demonstrated by paper chromatography in system (E).

C. robusta.—The dried and ground heartwood (550 g), collected at Anawhata, Auckland, was extracted (Soxhlet) with acetone (13 h) and then methanol (24 h). The concentrated acetone extract was poured into water and the precipitate (2.25 g) was repeatedly chromatographed from acetone to give (i) rubiadin 1-methyl ether (35 mg), m.p. and mixed m.p. 282—284° (with sublimation from 258°); (ii) rubiadin (0.44 g), m.p. and mixed m.p. 293—295°; (iii) an unidentified anthraquinone (52 mg), which crystallized from aqueous methanol as yellow needles, m.p. 244—245°, $\lambda_{max.}$ 238, 274, and 400 nm, $\nu_{max.}$ 3 390, 3 279 (β-OH), 1 670 (non-bonded conj. CO), and 1 635 cm^{-1} (bonded conj. CO) [the compound gave a pink colour with sodium carbonate solution, red with sodium hydroxide solution, and yellow-brown with concentrated sulphuric acid, and gave a positive reaction in the iron(III) chloride test]; acetate, lemon-yellow needles (from ethanol), m.p. 225° (with shrinking from 206°); and (iv) an unidentified anthraquinone (0.13 g) which was obtained as an amorphous solid, $\nu_{max.}$ 3 400 (β-OH), 1 658 (non-bonded conj. CO), and 1 639 cm^{-1} (bonded conj. CO) [the compound gave purple colourations with sodium carbonate and sodium hydroxide solutions, a deep red colour with concentrated sulphuric acid, and a positive reaction in the iron(III) chloride test].

The aqueous solution was extracted with ether to give traces of anthraquinones and scopoletin. The aqueous phase contained asperuloside, glucose, and an unidentified blue-fluorescing phenol.

Detection of Scopoletin in Coprosma *Species.*—Acetone extracts (10 h) of bark samples (5 g) (see Discussion for species) were examined by paper chromatography in systems (F) and (G) with authentic scopoletin as standard.

[6/347 *Received*, 18*th February*, 1976]