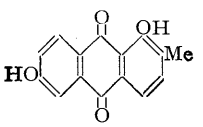
318. *Chemistry of the* Coprosma *Genus. Part VI.* Minor Anthraquinone Colouring Matters from* Coprosma australis.

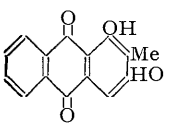
By Lindsay H. Briggs, G. A. Nicholls, and R. M. L. Paterson.

Three further compounds, soranjidiol, rubiadin, and a new dihydroxydimethoxymethylanthraquinone, have been isolated in small yield from the stem-bark of *Coprosma australis*. The new compound is shown to be copareolatin 1(or 5) : 6-dimethyl ether (*vide infra* for corrected nomenclature).

In working up the acetone extract of the stem-bark of *Coprosma australis* for its known constituents, morindin, morindone, and rubiadin 2-methyl ether (Part I, *J.*, 1948, 564) by chromatography on magnesia columns and using the displacement technique with acetic acid as described in Parts IV (*J.*, 1949, 1241) and V,* we have obtained, with difficulty, three further minor constituents. Two have been identified with the known compounds, soranjidiol (1 : 6-dihydroxy-2-methylanthraquinone) (I) and rubiadin (1 : 3-dihydroxy-2-methylanthraquinone) (II) respectively. The third compound is a new compound, $C_{17}H_{14}O_6$, containing two hydroxyl and two methoxyl groups, related to our " areolatin " † since complete methylation afforded the tetramethyl ether thereof (III). This new



(I)



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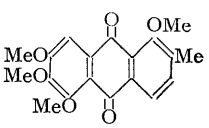


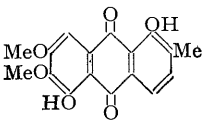
(III)

dimethyl ether is isomeric with copareolatin dimethyl ether prepared by partial methylation of copareolatin (Part II, *loc. cit.*), which we consider is the 6 : 7-dimethyl ether (IV). It dissolves in sodium carbonate solution, indicating a free β-hydroxyl group, and 80% sulphuric acid at 100° demethylates only one methoxyl group which must therefore be in

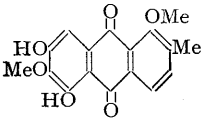
* Part V, *J.*, 1949, 1246.

† In Part II (*J.*, 1948, 568) a new compound, $C_{15}H_{10}O_6$, was isolated from *Coprosma areolata* and shown by degradation and synthesis (Part III, *J.*, 1948, 990) to be 1 : 5 : 6 : 7-tetrahydroxy-2-methylanthraquinone, for which the name areolatin was proposed. It was unfortunately not noticed, however, that the same name had been given by Hesse (*J. pr. Chem.*, 1903, **68**, 1) to a compound of unknown structure from *Pertusaria rupestris* [*P. communis* (β) *areolata*] with which it is not identical. We now propose the name copareolatin for the above compound from *Coprosma areolata*.

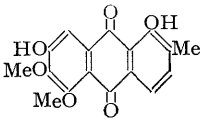
the α-position (cf. Graebe, *Annalen*, 1906, **349**, 211). These two facts, therefore, indicate the presence of methoxyl groups in α- and β-positions. Both the dimethyl ether and the monomethyl ether derived from it by demethylation are displaced by acetic acid on the magnesia column during chromatography, which indicates, in our experience, the absence of a vicinal dihydroxy-configuration. For these reasons, the dimethyl ether must be the 1(or 5) : 6-dimethyl ether (V) [or (VI)], while the monomethyl ether must be the 6-methyl ether (VII).



(IV)

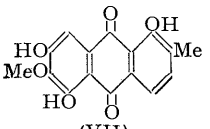


(V)

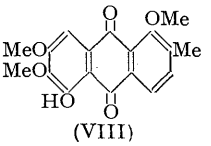


(VI)

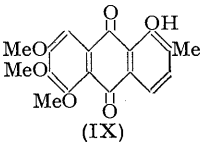
On chromatography of a preparation of copareolatin 6 : 7-dimethyl ether (Part II, *loc. cit.*), a trimethyl ether has been isolated, which is most probably the 1 : 6 : 7- or the 5 : 6 : 7-trimethyl derivative, (VIII) or (IX), the two β-hydroxyl groups undergoing methylation before the α-hydroxyl groups. From stereochemical considerations, however, the methoxyl group being larger than a methyl group, we suggest that, of the two α-hydroxyl groups, the one in the 1-position would be preferably methylated, leading to (VIII) for the trimethyl ether.



(VII)



(VIII)



(IX)

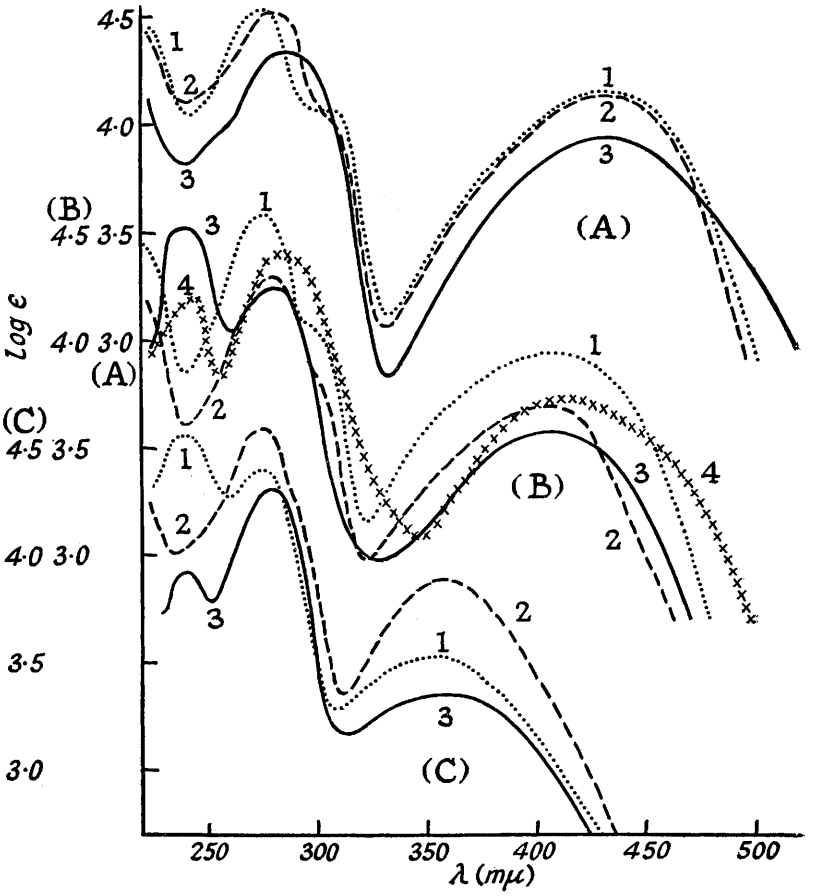
In an endeavour to differentiate between (V) and (VI) for the new dimethyl ether we have studied the ultra-violet absorption spectra of copareolatin and its methylated derivatives as well as the related anthragallol and its methylated derivatives. These measurements are recorded in the following table (λ in mμ) and in the figure.

	λ	log ε	λ	log ε	λ	log ε	λ	log ε	λ	log ε
Anthragallol 1 : 2-dimethyl ether	—	—	241	3·92	281	4·30	—	—	362·5	3·36
Anthragallol trimethyl ether	—	—	240	4·55	276·5	4·40	—	—	356	3·53
Copareolatin tetramethyl ether	—	—	—	—	276	4·59	—	—	358	3·88
Anthragallol	—	—	245·5	4·21	283·5	4·40	335 *	~3·21	413·5	3·72
,, 2-methyl ether	—	—	240	4·51	281·5	4·24	—	—	407·5	3·57
Copareolatin 1(or 5) : 6 : 7-trimethyl ether	—	—	—	—	276·5	4·57	300 *	~4·04	411	3·93
Copareolatin 1(or 5) : 6-dimethyl ether	—	—	—	—	281·5	4·29	—	—	407·5	3·68
Copareolatin	—	—	258 *	~3·96	288·5	4·34	—	—	432·5	3·92
,, 6-methyl ether	—	—	—	—	280	4·51	305 *	~4·05	432	4·11
,, 6 : 7-dimethyl ether	224·5	4·44	—	—	276	4·52	305 *	~4·04	427·5	4·13

* Inflexion.

Anthragallol and all of its derivatives exhibit an absorption band in the region 240—245·5 μ (log ε 3·92—4·55), not shown by copareolatin and its derivatives. This absorption is due to the chromophore $-C_6H_4\cdot COR$, one of the fundamental bands of anthraquinone itself (Morton and Earlam, *J.*, 1941, 159). A second band, also characteristic of this chromophore, is present only in the spectrum of anthragallol itself and then only as an inflexion at 335 mμ (log ε *ca.* 3·21). All compounds exhibit absorption in the region 276—288·5 mμ (log ε 4·24—4·59), characteristic of the quinonoid nucleus of anthraquinone itself (Morton and Earlam, *loc. cit.*). All the compounds exhibit a further broad absorption band due to the carbonyl group of the quinonoid nucleus, falling into three distinct groups at 356—362·5 (log ε 3·36—3·88), 407·5—413·5 (log ε 3·57—3·93), and 427·5—432·5 mμ (log ε 3·92—4·13). An inspection of the formulæ of these compounds reveals that the

common feature in the first group is that they contain no free α-hydroxyl group, in the second that they contain one free α-hydroxyl group, and in the third that they contain two such groups. Apparently this major band is greatly affected by the number of



Group A : 1. *Copareolatin* 6 : 7-*dimethyl ether.*
2. *Copareolatin* 6-*methyl ether.*
3. *Copareolatin.*

Group B : 1. *Copareolatin* 1(*or* 5) : 6 : 7-*trimethyl ether.*
2. *Copareolatin* 1(*or* 5) : 6-*dimethyl ether.*
3. *Anthragallol* 2-*methyl ether.*
4. *Anthragallol.*

Group C : 1. *Anthragallol trimethyl ether.*
2. *Copareolatin tetramethyl ether.*
3. *Anthragallol* 1 : 2-*dimethyl ether.*

α-hydroxyl groups, the presence of β-hydroxyl groups having little effect. Similar observations have been made by Morton and Earlam (*loc. cit.*).

It is not possible to differentiate between (V) and (VI) on the above data.

Experimental

The crude pigment from the stem bark of *Coprosma australis* was extracted with boiling acetone and cooled. A waxy substance separated which was removed before chromatography of the remaining acetone solution on six columns (4·5 × 16 cm.) of freshly calcined magnesia. At first the chromatogram resembled that described in Part I (*loc. cit.*) except that there was no band corresponding to morindin which had apparently been removed at an earlier stage. On development, however, and particularly on the addition of acetic acid (1—2 c.c. in 10—20 c.c.

of acetone) followed by further development with acetone, three relatively small bands were displaced with great difficulty from the strongly absorbed morindone band. The acetic acid drew the morindone down the column at the same time as the three smaller bands were displaced, making a clear cut separation impossible by a single absorption. The columns were extruded, and the three smaller, overlapping bands were cut out and finally separated into homogeneous bands by repeated chromatography on columns of decreasing size as described in Part IV (*loc. cit.*).

Band I : Morindone.—This was isolated and identified as described in Part I (*loc. cit.*).

Band II : Copareolatin 1(or 5) : 6-*Dimethyl Ether.*—The magnesia was removed from this band by dissolution in hydrochloric acid and the liberated pigment crystallised from glacial acetic acid (charcoal), forming orange hexagonal plates which darken, sublime, and sinter before melting at 271° (Found : C, 64·7; H, 4·4; OMe, 16·6. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5; 2OMe, 19·7%). The *compound* is soluble in 10% sodium hydroxide and sodium carbonate solutions with an orange-red colour, soluble in concentrated sulphuric acid with a violet colour, and gives a brown colour with ferric chloride solution.

The *diacetate* was prepared by momentarily warming over a water-bath a mixture of the dimethyl ether (24 mg.), acetic anhydride (0·5 c.c.), and 60% perchloric acid (1 drop) and pouring the whole into water 10 minutes later. The insoluble diacetate crystallised from alcohol in pale cream-coloured needles of constant decomposition point 131° when slowly heated (Found : C, 63·3; H, 4·5. $C_{21}H_{18}O_8$ requires C, 63·3; H, 4·55%).

The dimethyl ether was completely methylated with methyl sulphate and anhydrous potassium carbonate in acetone solution and formed pale yellow needles, m. p. 182—183°, when crystallised from alcohol, undepressed by an authentic sample of copareolatin tetramethyl ether, m. p. 184—185°. The latter compound was purified by chromatography and has a higher m. p. than that recorded in Part II (*loc. cit.*).

The dimethyl ether (90 mg.) was partly demethylated by 80% sulphuric acid (7 c.c.) for 1½ hours at 100° (cf. Graebe, *Annalen*, 1906, **349**, 222). At first the solution had a clear bright red colour but gradually a red precipitate was formed. The orange-yellow material obtained on dilution with water (10 c.c.) was dissolved in acetone and chromatographed on magnesia. Three bands were obtained : the small top band probably contained copareolatin ; the bottom band contained unchanged material (16 mg.), recovered as orange plates, m. p. 271—272°, from glacial acetic acid ; the intermediate red band afforded *copareolatin* 6-*methyl ether* (50 mg.), crystallising from glacial acetic acid in orange needles of constant m. p. 241° (Found : C, 64·2; H, 4·25. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0%). The monomethyl ether is soluble in 10% sodium hydroxide and sodium carbonate solutions with a red colour and gives a brown colour with ferric chloride.

Band III : Soranjidiol (1 : 6-*Dihydroxy*-2-*methylanthraquinone*).—The yellow pigment recovered from this band was repeatedly crystallised from glacial acetic acid, forming orange-yellow needles, m. p. and mixed m p. with 1 : 6-dihydroxy-2-methylanthraquinone *ex C. acerosa* (Part V, *J.*, 1949, 1246), 287—288°.

Band IV : Rubiadin (1 : 3-*Dihydroxy*-2-*methylanthraquinone*).—The yellow pigment recovered from this band crystallised from glacial acetic acid as yellow plates, m. p. and mixed m. p. with rubiadin, *ex C. lucida* (Part IV, *loc. cit.*), 297°. The acetate (cf. Part IV) crystallised from acetic anhydride as pale yellow needles, m. p. and mixed m. p. with rubiadin diacetate, 235°.

Band V : Rubiadin 1-*Methyl Ether.*—This was isolated and identified as described in Part I (*loc. cit.*).

Copareolatin 1(*or* 5) : 6 : 7-*Trimethyl Ether.*—A preparation of copareolatin 6 : 7-dimethyl ether (Part II, *loc. cit.*) was dissolved in acetone and chromatographed on magnesia. Three bands were obtained, two top red bands, one much darker than the other, but from both of which copareolatin 6 : 7-dimethyl ether was recovered, and an orange band. From the last band *copareolatin* 1(*or* 5) : 6 : 7-*trimethyl ether* was recovered and crystallised from alcohol as yellow needles of constant m. p. 177—178° (Found : C, 65·6; H, 5·2; OMe, 29·7. $C_{18}H_{16}O_6$ requires C, 65·8; H, 4·9; 3OMe, 28·4%). The trimethyl ether is insoluble in sodium carbonate solution but dissolves in 10% sodium hydroxide solution with a red colour and gives a brown colour with ferric chloride. On methylation with methyl sulphate and potassium carbonate in acetone solution it afforded copareolatin tetramethyl ether, crystallising from alcohol in pale yellow needles, m. p. 180°, undepressed by an authentic specimen.

The absorption spectra were measured in *ca.* N/20,000-alcoholic solution in a Beckman spectrophotometer, Model DU. All the compounds were rigidly purified by chromatography

from acetone solutions on magnesia columns until pure chromatograms were obtained, and then crystallised from appropriate solvents.

The analyses are by Drs. Weiler and Strauss, Oxford, Dr. T. S. Ma, Microchemical Department, Otago University, Dunedin, and Mr. R. N. Seelye of this department.

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