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THE HEARTWOOD CHROMONES OF *CEDRELOPSIS GREVEI*

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Abstract—The heartwood of *Cedrelopsis grevei* Baill. is shown to contain the known chromones heteropeucenin, alloptaeroxylin, ptaeroglycol, and peucenin. It also contains three new ones, greveichromenol, greveiglycol, and alloptaeroxylin methyl ether, and possibly a fourth, a methyl ether of greveiglycol which, however, may be an artefact. Greveichromenol is allocated structure (VIa) on spectroscopic grounds together with a conversion into isopeucenin. Greveiglycol (VIIIa) and the methyl ether (VIIIb) are allocated these structures on spectroscopic grounds together with syntheses from alloptaeroxylin methyl ether. A long range coupling is noted between the protons of the methyl group and the proton at position 3 in derivatives of 2-methylchromone, but it seems variable in magnitude and therefore of limited diagnostic value. Comparisons of the pyrones of divers samples of the heartwoods of *Cedrelopsis grevei* and of *Ptaeroxylon obliquum* show that these are closely related species but that their constituents are unsuitable for more detailed taxonomic purposes. *P. obliquum* has been found to contain peucenin 7-methyl ether, overlooked in the earlier study, and not previously encountered as a natural product.

RESULTS AND DISCUSSION

SOME time ago, the heartwood constituents of *Ptaeroxylon obliquum*, the African sneezewood, were examined in the hope that they would clarify certain taxonomic relationships left obscure by purely morphological criteria.[1-3] However, two samples of wood from different sources gave rather different results, neither agreeing well with the pattern from a third sample studied by other workers with a similar object.[4-6] The heartwood of Madagascan *Cedrelopsis grevei* Baill. was also reported[2b] to contain ptaeroxylin (desoxykarenin) while a new coumarin, cedrelopsin, has been reported[7] more recently and shown to have structural affinities with the coumarins from *P. obliquum*. These observations induced us to examine *C. grevei* more closely as a general test of the validity of the heartwood pyrones as taxonomic markers. Professor D. A. H. Taylor kindly sent us the extracts of the wood he had used, together with another sample of the wood itself. The presence of ptaeroxylin and cedrelopsin in the extracts has been confirmed, and alloptaeroxylin and peucenin have also been found,[8] thus strengthening the parallel with *P. obliquum*. But the wood, while again containing chromones typical of *P. obliquum*, supplied a different selection besides three (and possibly four) chromones not known before. The five samples are compared in Table 1, from which it is clear that they are all related in that they contain 2-methylchromones (not yet very common), some 2-hydroxymethylchromones (rare), several oxepin derivatives (very rare), and a number of derivatives (a few of usual, some rare types) of aesculetin.

[1] F. M. DEAN and D. A. H. TAYLOR, *J. Chem. Soc.* C, 114 (1966).
[2] F. M. DEAN, B. PARTON, N. SOMVICHIEN and D. A. H. TAYLOR, *Tetrahedron Letters* (a) 2147; (b) 3459 (1967).
[3] F. M. DEAN, B. PARTON, A. W. PRICE, N. SOMVICHIEN and D. A. H. TAYLOR, *Tetrahedron Letters* 2737 (1967).
[4] P. H. MCCABE, R. MCCRINDLE and R. D. H. MURRAY, *J. Chem. Soc.* C, 145 (1967).
[5] M. M. BALLANTYNE, R. D. H. MURRAY and A. B. PENROSE, *Tetrahedron Letters* 4155 (1968).
[6] R. D. H. MURRAY and M. M. BALLANTYNE, *Tetrahedron Letters* 4031 (1969).
[7] I. T. ESHIETT and D. A. H. TAYLOR, *J. Chem. Soc.* C, 481 (1968).
[8] N. SOMVICHIEN, unpublished work.

TABLE 1. THE INCIDENCE OF HEARTWOOD PYRONES IN VARIOUS SAMPLES OF *Cedrelopsis grevei* AND OF *Ptaeroxylon obliquum*

	C. grevei		*P. obliquum*		
	A	B	C	D	E
8-Substituted Chromones					
Heteropeucenin	3·59†			2·81	3·00
Heteropeucenin 7-methyl ether				3 88	2 70
Heteropeucenin dimethyl ether				3·59	
Alloptaeroxylin	4·04	2·26[8]			3·18
Alloptaeroxylin methyl ether	4·26				
Greveiglycol	1·79				
Greveiglycol 4′-methyl ether	0·60				
Ptaerochromenol*					3·40
6-Substituted Chromones					
Peucenin	1·93	2·22[8]	3·3	3·13	2·86
Peucenin 7-methyl ether				2·98	
Umtatin*				3·79	3·00
Greveichromenol*	2·37				
6-Substituted Chromones Derived from Oxepin					
Ptaeroxylin[1, 2b] (desoxykarenin[4])		4·02[2b, 7]	1·60	1·18	3·38
Dehydroptaeroxylin				1·56	
Karenin			2·30		
Ptaeroxylinol*					4·06
Ptaeroglycol	1·81				3·20
Ptaerocyclin					2·10
Ptaeroxylone					1·70
Coumarins					
Nieshoutin[4, 5] (cyclo-obliquetin[2a])			2·18		2·88
Cedrelopsin		2·04[7, 8]			
Nieshoutol			3·36		
Scopoletin					1·67
Prenyletin				1·13	1·68
7-*O*-3,3-dimethylallylscopoletin			2·40		
7-*O*-1,1-dimethylallylscopoletin			2·46		
Obliquin				3·48	2·88
Obliquol				3·08	3·00
Obliquetol				1·45	3·00
Obliquetin					2·44

A. This work. B. Wood extracted in Ibadan. C. Wood extracted in Glasgow. D. Wood from Kokstad. E. Wood from Lushoto.

* Distinguishes a derivative of 2-hydroxymethylchromone.

† To give manageable figures, yields are expressed as $\log_{10}$ (mg compound/100 g wood).

Certainly, such results support in a general way the view that the two species are more closely related to each other than to, say, those of the Meliaceae, and that they should be placed in a small, separate family, the Ptaeroxylaceae.[1, 2b] On the other hand, the variations preclude the use of these compounds for more detailed taxonomic work unless, indeed, they arise from the interbreeding of very closely related plants.

The chief constituents of the wood of *C. grevei* were heteropeucenin (Ia), alloptaeroxylin (IIa), and alloptaeroxylin methyl ether (IIb). The last is new and was recognized spectroscopically and identified by demethylation using boron chloride. The yield of alloptaeroxylin (IIa) was very poor because of the polymerization suffered by the acid-sensitive

chromene system, so the result was confirmed by hydrogenating the new compound first and then demethylating it to isoheteropeucenin (IIIa).

The minor constituents included the known compounds peucenin[9] (IVa) and ptaeroglycol[2b] (V) along with two new ones. That named greveichromenol has structure (VIa) and gives positive ferric and Gibbs' tests while the NMR spectrum is clearly indicative of a 2,2-dimethylchromene nucleus, one aromatic proton, one pyrone proton, and a methylene group. Since, moreover, the IR and UV spectra correspond to a chromone system the fact that the compound reduces Fehlings' reagent provides strong evidence for the presence of the 2-hydroxymethylchromone grouping.[3] Finally, the structure was confirmed by converting the compound into isopeucenin (VII). Treatment with mesyl chloride in pyridine transformed greveichromenol not into the mesylate but into the halide (VIc), behaviour noted before[3] and probably a consequence of an exceptionally easy nucleophilic substitution of mesylate by chloride ion. Hydrogenation removed the halogen and saturated the ethylenic link to produce isopeucenin[9] (VII) identical with a specimen made by cyclization of peucenin (IVa).

The other new constituent appeared from its IR and UV spectra to be a chromone containing hydroxyl groups but the absence of solubility in alkali and of a ferric reaction showed that no phenolic group was present. The compound was sensitive to periodic acid (though no product could be isolated) and the existence of a 1,2-glycol grouping inferred. The NMR spectrum exhibited three distinct methyl bands aside from a methoxyl methyl band thus encouraging the belief that one of the glycols (VIIIa) and (IX)* was in hand, while the spectrum of the diacetate revealed splitting between one methyl group and the pyrone proton, a type of long range coupling that is to be expected in 2-methylchromone nuclei though we find it to vary in magnitude in a manner not understood (Table 2). The

TABLE 2. NMR SPECTRA*

		5-OH	2'-Me	2-Me	OAc	OMe	ArH	3-H	3'-H	4'-H	Solvent
Alloptacroxylin methyl ether	IIb		8·52 (6H) *J* 1	7·68d		6·05	3·68	3·26q *J* 1	4·41q *J* 10	4·41d *J* 10	$CDCl_3$
Isoheteropeucenin methyl ether	IIIb		8·61 (6H) *J* 0·8	7·69d		6·07	3·68	3·95q *J* 0·8	8·14t *J* 6·6	7·20t *J* 6·6	$CDCl_3$
Heteropeucenin 7-acetate	Ic	−2·62	8·29 8·20	7·61	7·67		3·49	3·91			$CDCl_3$
Greveichromenol acetate	VIb	−2·78	8·57	5·10br (2H)	7·85		3·76	3·85br	4·46d *J* 10	3·35 *J* 10	$CDCl_3$
Greveiglycol	VIIIa		8·68, 8·63	7·73		6·29	3·76	4·12	6·45m	4·72m	d_6-DMSO
Greveiglycol diacetate	VIIIa OAc for OH		8·56 8·49	7·78d *J* 0·8	7·87 (6H)	6·07	3·68	3·98q *J* 0·8	4·82d *J* 3·4	3·84d *J* 3·4	$CDCl_3$
Cis-glycol	IX		8·63, 8·61	7·72br		6·26	3·73	4·08br	6·41dd *J* 4·5,† 7·5‡	5·18dd *J* 4·5,† 4·5‡	d_6-DMSO
Greveiglycol methyl ether	VIIIb		8·65, 8·59	7·75br		6·28	3·73	4·06br	6·11d *J* 3	5·62d *J* 3	d_6-DMSO (with HCl)

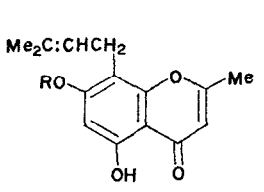
* τ Scale, with T.M.S. as internal standard
† Dihedral coupling in CH–CH.
‡ Dihedral coupling in CH–OH.

* These structures do not imply absolute configurations, which are unknown.

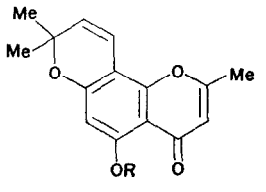
[9] E. SPÄTH and K. EITER, *Chem. Ber.* **74**, 1851 (1941); A. BOLLETER, K. EITER and H. SCHMID, *Helv. Chim. Acta* **34**, 186 (1951).

references[4] in the literature to such bands as 'singlets' must be taken as an over-simplification. The same spectrum suggested the *trans* orientation (VIIIa) for the glycol system, the dihedral coupling constant being about 3 Hz as in comparable glycols in the coumarin series.[10] In confirmation, both *cis* and *trans* glycols were synthesized, and the new compound, now named greveiglycol, fully identified with the *trans* isomer (VIIIa).

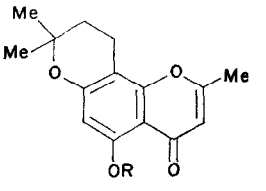
Firstly, alloptaeroxylin methyl ether (IIb) and osmium tetroxide supplied an osmate that was hydrolysed by cold alkali in the presence of mannitol; despite the sensitive character of



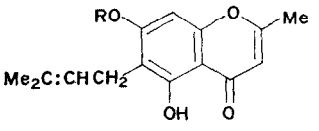
(Ia) R = H
(Ib) R = Me
(Ic) R = Ac



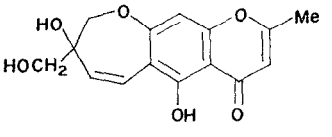
(IIa) R = H
(IIb) R = Me



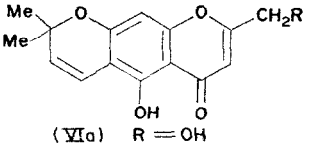
(IIIa) R = H
(IIIb) R = Me



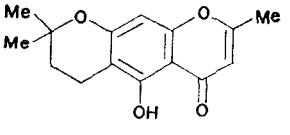
(IVa) R = H
(IVb) R = Me



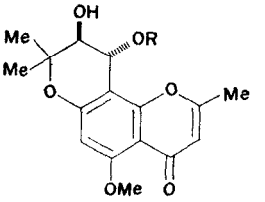
(V)



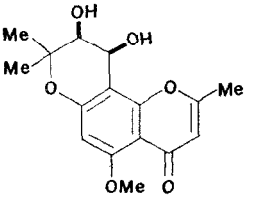
(VIa) R = OH
(VIb) R = OAc
(VIc) R = Cl



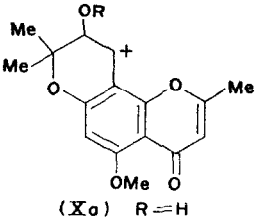
(VII)



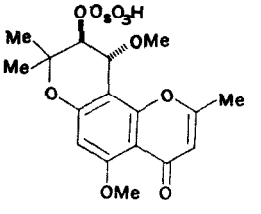
(VIIIa) R = H
(VIIIb) R = Me



(IX)



(Xa) R = H
(Xb) R = OSO_3H



(XI)

its nucleus, the *cis*-glycol (IX) was obtained in about 50% yield and the stereochemistry confirmed by the dihedral coupling constant of 4·5 Hz, again comparable with that in equivalent model systems.[10] Although hydrochloric acid in warm aqueous acetone catalysed a change to the *trans*-glycol, presumably via the benzylic carbonium ion (Xa), other products preponderated and the method was rejected. The desired *trans*-glycol was then

[10] F. BOHLMANN, V. S. BHASKAR RAO, and M. GRENZ, *Tetrahedron Letters* 3947 (1968).

obtained by oxidation of the ether (IIb) with 3-chloroperbenzoic acid followed by hydrolysis with aqueous oxalic acid.

The last compound isolated from the wood was the methyl ether (VIIIb) of greveiglycol. The yield was very small, and it seems likely that the compound is merely an artefact produced from greveiglycol during manipulations, since even the most careful work could not wholly exclude either adventitious traces of acids which would induce carbonium ion formation or of methanol or other methylating agents which would react with the carbonium ion giving (VIIIb). As too little was available for NMR studies, the compound was recognized from the UV, IR and mass spectral studies and identified by synthesis. The osmic ester from alloptaeroxylin methyl ether was converted smoothly and directly into the desired product by treating it with hydrochloric acid to produce carbonium ion (Xb) in the presence of methanol to allow formation of the *trans* derivative (XI) and then (VIIIb) by hydrolysis. The point of this procedure is that acyclic osmates are easily hydrolysed, and the method therefore avoids the usual but troublesome methods of removing osmium from the more stable cyclic esters.

EXPERIMENTAL

Molecular weights were determined mass spectroscopically, IR spectra were measured on paraffin mulls or on KBr discs. UV spectra were determined upon solutions in 95% EtOH at concentrations between 10^{-3} and 10^{-4} M. Gibbs and oth[redacted] tests were conducted as described previously.[2b, 3]

The wood used was supplied by Professor D. A. H. Taylor, Ibadan University, Nigeria, having been collected by Herr G. Schmid, Basel, and herbarium specimens having been preserved as G. Schmid No. 52 in the Forest Herbarium, Oxford.

Extraction and isolation procedure. The heartwood of *Cedrelopsis grevei* was reduced to shavings on a lathe and the shavings (1 kg) extracted in a Soxhlet apparatus successively with (i) light petroleum (b.p. 40–60°) (5 l.) for 6 hr, (ii) light petroleum (b.p. 60–80°) (5 l.) for 24 hr, (iii) Et_2O (5 l.) for 24 hr, (iv) benzene (4 l.) for 24 hr, and (v) MeOH (4 l.) for 16 hr. The extracts were treated as follows.

Extract (i) was concentrated to a yellow gum (15·6 g) which was subjected to fractional crystallization from MeOH. The earliest crops consisted mainly of alloptaeroxylin. The third crop consisted mainly of an aliphatic ester and was rejected. After 6 crops, little alloptaeroxylin remained in the mother liquors which were then evaporated to a gummy residue A carried into the next stage of separation. After further recrystallization, the alloptaeroxylin (5·8 g) had m.p. 154–155°.

Extract (ii) was concentrated to 500 ml and when left supplied a gum that partly crystallized from MeOH giving alloptaeroxylin. Concentration of the mother liquors gave a gum B which, combined with A from (i), formed an oil (25·3 g) and was chromatographed on silica (750 g). Elution began with benzene and the first fractions contained mainly an aliphatic ester that was discarded. Elution was continued with benzene containing gradually increasing amounts of $CHCl_3$ until the ratio was 1:1. Evaporation of these fractions supplied crude alloptaeroxylin which was purified from MeOH. Continued elution with the benzene–$CHCl_3$ ratio changing from 1:1 to 1:4 gave eluates that, when evaporated and crystallized from benzene, gave alloptaeroxylin methyl ether. A mixture of at least eight substances was finally eluted by pure $CHCl_3$, but no single compound could be isolated. All mother liquors were recombined and their contents re-chromatographed in the same way to give further quantities of alloptaeroxylin and its methyl ether. After that, the residues partly crystallized from MeOH affording greveichromenol as plates from MeOH and then benzene. The alloptaeroxylin obtained totalled 4·8 g, the methyl ether 9·3 g, and the greveichromenol, 0·3 g.

Extract (iii) upon evaporation supplied a gum (45 g) that did not solidify but partly crystallized from MeOH giving a solid B consisting of a mixture of heteropeucenin and alloptaeroxylin methyl ether which were separated by treating the solution in $CHCl_3$ very quickly with 2*N* NaOH. The alkaline extract was at once acidified and the heteropeucenin (2·2 g) collected into $CHCl_3$, while the alloptaeroxylin methyl ether (2·3 g) was obtained by washing its solution with H_2O, evaporating the solvent, and crystallizing the residue from benzene. The methanolic mother liquors from solid B were evaporated and the residue chromatographed on silica (900 g) beginning with benzene for elution. Benzene alone eluted first an oil (rejected) and then alloptaeroxylin. Benzene–$CHCl_3$ (4:1) then eluted an amorphous solid that crystallized from benzene giving peucenin (65 mg). Next, benzene–$CHCl_3$ (1:1) was used to elute a mixture of alloptaeroxylin methyl ether (0·5 g) and greveichromenol (114 mg). Elution was completed with $CHCl_3$–MeOH (19:1) which removed a reddish gum that deposited ptacroglycol (64 mg) when kept in acetone–light petroleum for 1 week. All residues from this column were combined to form gum D (16·5 g) which was washed briefly with acetone to

remove a mixture (1 g) of alloptaeroxylin methyl ether and greveichromenol and then chromatographed on alumina (neutral, with 3% water; 480 g) whence benzene eluted alloptaeroxylin methyl ether (3·3 g) followed by greveiglycol (17 mg), peucenin (20 mg), and greveiglycol methyl ether (4 mg) as the concentration of $CHCl_3$ increased.

Extract (iv) gave upon concentration a brown gum (22·3 g). Trituration with Et_2O eventually supplied a yellow powder which, when washed with acetone, supplied greveiglycol (44 mg). Re-chromatography of the rest of the material from this extract gave more alloptaeroxylin methyl ether (0·5 g).

Extract (v) formed a gum (73·5 g) containing about 1% each of alloptaeroxylin and its methyl ether. Efforts to obtain other pure compounds failed.

Alloptaeroxylin (IIa). This separated from MeOH as yellow needles (10·9 g), m.p. 152–155°, identical with authentic material.

Alloptaeroxylin methyl ether (IIb). This *ether* crystallized from benzene as needles (18·4 g), m.p. 155–157°, that were insoluble in dil. NaOH solution and gave neither ferric nor Gibbs' tests. (Found: C, 70·3; H, 5·9%; *M* 272. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%; *M* 272.) This compound had λ_{max} 225(sh), 240(sh), 258(sh), 263, 294(sh), and 331 nm. (log ϵ 4·21, 4·31, 4·56, 4·59, 3·73, 3·70) and ν_{max} 1670 (chromone CO), 1630, 1605, 1575 $cm.^{-1}$

Demethylation of this ether (0·5 g) in CH_2Cl_2 (5 ml) was effected with BCl_3 (1·7 g) in the same solvent (5 ml) at −4° during 25 min. An excess of NaOAc solution was added and the product, isolated by evaporation of the CH_2Cl_2 layer, was chromatographed on silica using benzene. This gave alloptaeroxylin (20 mg), m.p. 152–154° identical with authentic material.

Isoheteropeucenin methyl ether (IIIb). Alloptaeroxylin methyl ether (1 g) in HOAc (50 ml) was shaken with Pd/C (10%; 0·2 g) under H_2 at room temp. and pressure. The reaction was complete in 5 min, and the solution was filtered and evaporated. The oily product solidified in contact with Et_2O giving a product (0·8 g) that when crystallized from benzene supplied *isoheteropeucenin methyl ether* as needles m.p. 157–158°, λ_{max} 231, 250, 257, and 290 nm (log ϵ 4·18, 4·33, 4·36, 3·93), ν_{max} 1665 (chromone C:O), 1630, 1610, 1590 cm^{-1}. (Found: C, 70·3; H, 6·7%; *M*, 274. $C_{16}H_{14}O_8$ requires C, 70·1; H, 6·6%; *M*, 274.)

This ether (0·1 g) in CH_2Cl_2 (10 ml) was treated at −70° with BCl_3 (1 ml) and the mixture left to warm to 20°; it was then added to aqueous NaOAc and the organic layer was diluted with Et_2O. Removal of the organic solvents left a solid that was purified on a column of silica with elution by benzene, gradually changing to $CHCl_3$, and then crystallized from MeOH giving isoheteropeucenin (IIIa) (40 mg), m.p. 230°, identical with an authentic specimen.

Peucenin (IVa) This formed needles, m.p. 210–211°, identical with authentic material.

Ptaeroglycol (V). This formed a pale yellow amorphous solid, m.p 235°, identical spectroscopically with an authentic sample.

Heteropeucenin (Ia). This formed fine, faintly yellow needles, 185–188°, identical with an authentic specimen. Partial methylation was effected with Me_2SO_4 in boiling acetone containing K_2CO_3 and gave the 7-methyl ether (Ib), m.p. 105–109°, identical with an authentic sample. Acetylation with Ac_2O and pyridine at 25° for 40 min. gave *heteropeucenin 7-acetate* (Ic), which separated from MeOH as fine needles, m.p. 109–112°, ν_{max} 1745 (ArOAc), 1660 (chromone C:O) cm^{-1}. (Found: C, 67·4; H, 5·8%; *M*, 302. $C_{17}H_{18}O_5$ requires C, 67·6; H, 6·0%; *M*, 302.)

Greveichromenol (VIa). Greveichromenol formed shiny, slightly cream coloured plates from benzene or yellowish prisms from MeOH and in either case had m.p. 186°, gave an intense green ferric reaction and a positive reaction with Gibbs' reagent and with Fehlings' reagent though it was not very soluble in dil. NaOH, and had λ_{max} 231, 249, 276, 300(sh), and 318(sh) nm (log ϵ 4·27, 4·18, 4·50, 4·03, 3·81), and ν_{max} 3330 (OH), 1660 (chromone C:O), 1630 and 1580 cm^{-1}. (Found: C, 65·4; H, 5·2%; *M*, 274. $C_{15}H_{14}O_6$ requires C, 65·7; H, 5·2; *M*, 274.)

Acetylation of greveichromenol (50 mg) with Ac_2O (2 ml) and pyridine (0·05 ml) at 25° for 2 hr, and purification of the product from MeOH, gave the *monoacetate* (VIb) as needles, m.p. 139–140°, ν_{max} 1745 (CH_2OAc), 1660 (chromone CO), 1630 and 1595 cm^{-1}, giving an emerald green ferric reaction. (Found: C, 64·7; H, 5·3%; *M*, 316.)

Greveichromenol was converted into isopeucenin as follows. The compound (57 mg) in pyridine (2·4 ml) was treated with mesyl chloride (0·04 ml) at 0° for 4 hr and then stirred into ice. The precipitate crystallized from MeOH as plates (24 mg), m.p. 149–151°, showing in the mass spectrometer molecular ions at 292 and 294 indicative of chlorine isotopes. As the compound was unstable it was not examined further but a sample (16 mg) was at once shaken in EtOAc (10 ml) with Pd/C (10%; 10 mg) under H_2 at ambient temperature and pressure Purified from light petroleum (b.p. 60–80°), the product supplied isopeucenin as needles (7 mg), m.p. 129–131°, identical with a sample prepared from peucenin in a known fashion.[9]

Greveiglycol (VIIIa). *Greveiglycol* separated from MeOH as tiny needles, m.p. 282–283°, soluble in Me_2SO but hardly in acetone, $CHCl_3$, or benzene, and having λ_{max} 249, 256, 289 nm (log ϵ 4·43, 4·44, 4·09), ν_{max} 3490 (OH), 1655 (chromone CO), 1615, and 1580 cm^{-1}. (Found: C, 62·5; H, 6·1%; *M*, 306. $C_{16}H_{18}O_6$ requires C, 62·7–H, 5·9%; *M* 306.) Formed by the use of Ac_2O and pyridine at 80° for 1 hr, the *diacetate* had m.p. 222–226° (decomp.) (from Et_2O), and absorbed at 1748 (alkyl acetate), 1665 (chromone CO), 1608, and 1590 cm^{-1}. (Found: C, 61·4; H, 5·6%; *M*, 390. $C_{20}H_{22}O_8$ requires C, 61·5; H, 5·7%; *M*, 390.)

Oxidations of alloptaeroxylin 5-methyl ether. (i) The ether (0·5 g) was left for a day with 3-chloroperbenzoic acid (3 g) in $CHCl_3$ (25 ml) in the dark. The acids were washed out with dil. $NaHCO_3$ and the solvent evaporated leaving a gum that was boiled with 2% aqueous oxalic acid (100 ml.) for 100 min. As it cooled, the solution deposited crystals (0·15 g) of a *trans*-glycol identified by spectroscopic, chromatographic, and mixed m.p. techniques with greveiglycol. (ii) During 5 days at room temp., a mixture of the ether (0·1 g) and OsO_4 (0·1 g) in tetrahydrofuran (6 ml) deposited a black solid. Evaporation of the solvent left a residue that was dissolved in $CHCl_3$ (5 ml) and shaken for 3·5 hr with a solution of mannitol (0·4 g) and NaOH (0·15 g) in H_2O (15 ml). Now colourless, the organic layer was washed (H_2O) and evaporated to a solid that crystallized from MeOH yielding the *cis-glycol* (IX) as tiny needles (53 mg), m.p. 231–232°, with a UV absorption identical with that of greveiglycol but with ν_{max} 3460 and 3300 (OH), 1660 (chromone CO), 1605 and 1585 cm^{-1}. (Found: C, 62·6; H, 5·8%; *M*, 306. $C_{16}H_{18}O_6$ requires C, 62·7; H, 6·9; *M*, 306.) (iii) The ether (0·091 g) was oxidized as before with OsO_4 (0·1 g) in tetrahydrofuran, but the resulting black osmate was treated with MeOH (5 ml) through which HCl was bubbled for 1 min. The mixture was kept at room temp. until its colour faded to yellow, whereafter the solution was concentrated and cooled. This gave first a little greveiglycol (7 mg) and then *greveiglycol 4'-methyl ether* (VIIIb) crystallizing as micro-needles, m.p. 235–240°, devoid of a ferric reaction but having λ_{max} 248, 255, and 288 nm (log ϵ 4·32, 4·33, 3·98), ν_{max} 3390 (OH), 1655 (chromone CO), 1610 and 1585 cm^{-1}. (Found: C, 63·7; H, 6·1%; *M*, 320.12594. $C_{17}H_{20}O_6$ requires C, 63·7; H, 6·3%; *M*, 320·12598.)

Peucenin 7-methyl ether (Ib). Residues from the extraction and chromatography of the heartwood (1·6 kg) of *P. obliquum* obtained from Kokstad were retained from the work described previously[1] and extensively re-chromatographed on silica columns. Fractions formerly thought to contain only heteropeucenin ethers yielded peucenin derivatives also. *Peucenin 7-methyl ether* was obtained as needles (1·9 g), m.p. 109°, identical with a sample prepared from peucenin.[2a, 9] This ether has not been recognised as a natural product before.