THE CHEMISTRY OF THE PTAEROXYLACEAE.

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ABSTRACT:
Compounds isolated from the Ptaeroxylaceae family are discussed. The similarity of compounds isolated from *Ptaeroxylon obliquum* and *Cedrelopsis grevei* of the Ptaeroxylaceae family and from *Cneorum tricoccon* and *Neochamaelea pulverulenta* of the Cneoraceae family suggests a very close relationship between these families.

INTRODUCTION

The Ptaeroxylaceae is a small family comprising two genera, *Ptaeroxylon,* a monotypic genus comprising only the southern African species *Ptaeroxylon obliquum,* commonly known as sneezewood, and *Cedrelopsis* a genus, which only occurs in Madagascar. *Ptaeroxylon* has been placed in the Sapindaceae, the Rutaceae, and most commonly, in the Meliaceae family. The grouping together of *Ptaeroxylon* and *Cedrelopsis* was supported by chemical evidence, both *Cedrelopsis grevei and Ptaeroxylon obliquum* were shown to contain a wide variety of chromones (Figure 1) and coumarins (Figure 2) [1,2,3,4,5,6,7], but no limonoids, which are the compounds commonly found in the Meliaceae. Pennington and Styles grouped *Cedrelopsis* and *Ptaeroxylon* together and placed them in a distinct family, the Ptaeroxylaceae [8].

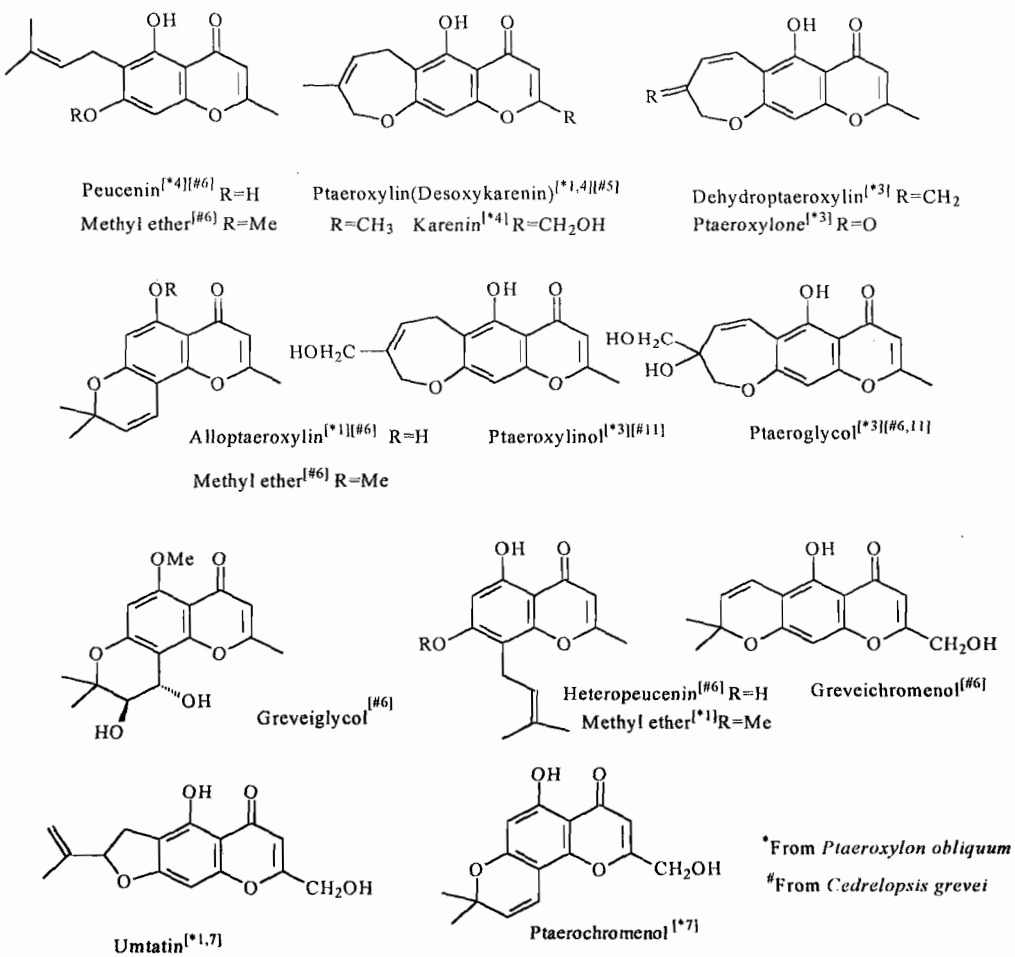
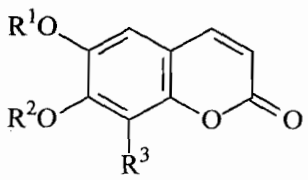


Fig. 1. Chromones from *C.grevei*# *and P. obliquum**



Compound	R^1	R^2	R^3	Ref.
Scoparone#	Me	Me	H	[9,11]
Scopoletin*	Me	H	H	[2,9]
7-O-(3,3-dimethylallyl)scopoletin*	Me	$(CH_3)_2C=CHCH_2$-	H	[4]
7-O-(1,1-dimethylallyl)scopoletin*	Me	H	$CH_2=CH(CH_3)_2C$-	[4]
Obliquetin*	Me	H	$CH_2=CH(CH_3)_2C$-	[2]
Obliquetol*	H	H	$CH_2=CH(CH_3)_2C$-	[2]
Cedrelopsin#	Me	H	$(CH_3)_2C=CHCH_2$-	[5,11]
O-Methylcedrelopsin#	Me	Me	$(CH_3)_2C=CHCH_2$-	[10,11]
7-O-(3,3-dimethylallyl)aesculetin*	H	$(CH_3)_2C=CHCH_2$-	H	[2]

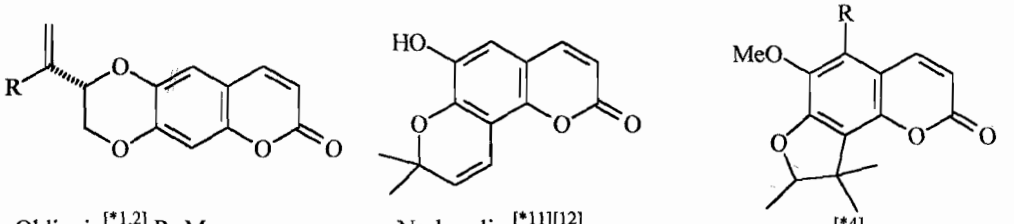


Fig. 2. Coumarins from *C. grevei*# and *P. obliquum**

CHROMONES AND COUMARINS

Chromones isolated from the Ptaeroxylaceae are typically 5,7-dioxygenated with a single prenyl group at either C-6 or C-8 which may, or may not, be incorporated into a third ring, which may be 5, 6, or 7-membered. The methyl group at C-2 may be converted into a primary alcohol. The chromones isolated previously from the Ptaeroxylaceae are shown in Figure 1.

Coumarins are typically 6,7-dioxygenated and may have a prenyl substituent at C-8 (as in obliquetin) or at the C-7 oxygen [as in 7-O-(3,3-dimethylallyl) aesculetin]. The coumarins isolated previously from the Ptaeroxylaceae are shown in Figure 2.

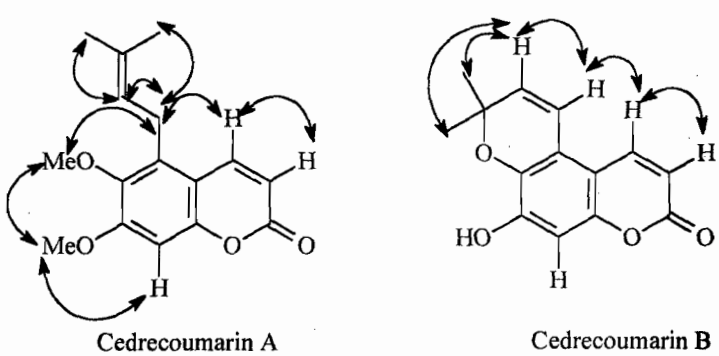


Fig. 3. Coumarins from *Cedrelopsis grevei*

RECENT INVESTIGATIONS

A re-investigation of the bark of a specimen of *Cedrelopsis grevei* from the dry south–west of Madagascar yielded β-amyrin as the major constituent, and yielded the chromones ptaeroglycol and ptaeroxylinol and the coumarins, cedrelopsin, scoparone, o-methylcedrelopsin, norbraylin and two coumarins, cedrecoumarins a and b which have not been described previously [11]. These compounds are unusual in being prenylated at C-5. Structures of these compounds were confirmed using NOE difference experiments as shown in figure3.

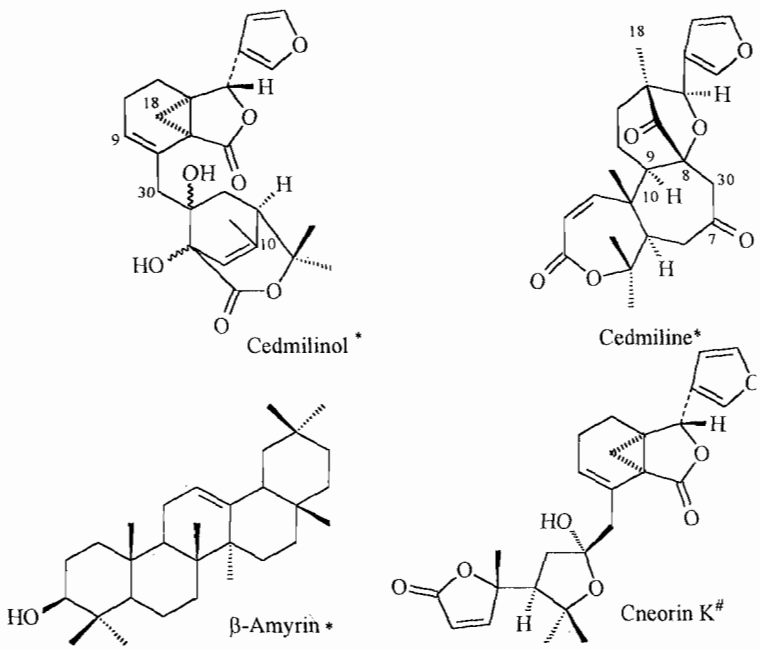


Fig. 4. Triterpenoid and limonoid derivatives from *Cedrelopsis grevei** (Ptaeroxylaceae) *and Neochamaelea pulverulenta#* (Cneoraceae).

TRITERPENOID DERIVATIVES FROM *CEDRELOPSIS.*

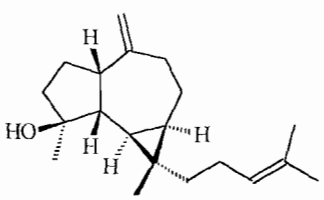
The stem bark of a specimen of *Cedrelopsis grevei* collected in the wetter north-west of Madagascar was investigated and the common triterpenoid, β-amyrin and two novel limonoid derivatives, the pentanortriterpenoid, cedmilinol and the hexanortriterpenoid, cedmiline were isolated [13]. A literature search showed that these limonoid derivatives most closely resemble those reported previously from the Cneoraceae, for example cneorin K from *Neochamaelea pulverulenta* [14]. In both cneorin K and cedmilinol, ring D has been contracted, the methyl group at C-30 has been incorporated between C-8 and C-7 and the C-9, C-10 bond has been cleaved. Rings A and B have been modified.

A literature search revealed that prenylated and diprenylated coumarins are common in the Cneoraceae [15]. Cedrelopsin has been isolated from *Cedrelopsis grevei* [5,11], and *Neochamaelea pulverulenta* [16] and ptaerochromenol has been isolated from *Ptaeroxylon obliquum* [7] and the 5-methyl ether derivative from *Cneorum tricoccon* [17]. Also ptaeroglycol has been isolated from *Cedrelopsis grevei* [6,11], *Ptaeroxylon obliquum* [3] and *Neochamaelea pulverulenta* [18].

The Cneoraceae family comprises two genera with a total of three species. *Neochamaelea pulverulenta* (syn *Cneorum pulverulentum*) occurs in the Canary Islands and *Cneorum tricoccon* occurs in the coastal areas of the western Mediterranean. The third species, *Cneorum trimerum* occurs in Cuba and doesn't appear to have been investigated chemically [19]. It is interesting that the Cneoraceae, like the Ptaeroxylaceae has also been assigned to the Sapindaceae and the Rutales at different times [20,21,22,23].

An Unusual Aromadendrane Diterpenoid From *Ptaeroxylon obliquum.*

It was decided to re-investigate the bark of *P. obliquum* [24] to see whether similar limonoid derivatives could be found. However, only one compound, the diterpenoid, cneorubin X was isolated from this source. It is interesting that this compound has been reported only twice previously, once from *Cneorum tricoccon* [25] and secondly from a marine sponge of the *Sinularia* genus [26]. The occurrence of this compound in *Ptaeroxylon obliquum* provided a third indication of a close relationship between the Ptaeroxylaceae and the Cneoraceae families.



Scheme 3. Cneorubin X from *Ptaeroxylon obliquum*, *Cneorum tricoccon* and *Sinularia* genus.

CONCLUSION

The presence of similar limonoid derivatives, coumarins and chromones, and an unusual diterpenoid in the Ptaeroxylaceae and Cneoraceae shows that the Ptaeroxylaceae are more similar in chemical constituents to the Cneoraceae than to the Meliaceae with which it was thought to be most closely related. The isolation of the two unusual complex limonoid derivatives suggests that the Ptaeroxylaceae, and in particular the seed which has not been examined, should be further investigated in search of these interesting compounds.

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