

PHENYLPROPANOIDS IN ALKALOID-FREE SPECIES OF *PHOEBE*

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We recently reported (1-3) on aporphine alkaloids from two Costa Rican species of *Phoebe* (Lauraceae) and now describe the major components of two additional species that do not accumulate alkaloids. The stem bark of *Phoebe mexicana* Meissn. yielded 0.01% of the lignan (+)-sesamin (optical rotation, mp, uv, ^1H and ^{13}C nmr, ms) in comparison with a known sample (4) and 0.015% (-)-epicatechin (optical rotation, mp, ir, ms, ^1H - and ^{13}C -nmr spectra) compared with the literature values. More interesting were the results on *Phoebe brenesii* Standley. Stem bark yielded 0.22% crystalline *trans*-3'-methylsulphonylallyl *trans*-cinnamate (**1**) while wood yielded traces of **1** along with 0.3% benzyl *trans*-cinnamate. The latter was identified by synthesis and the former by comparison of mp, ir, ms, and ^1H nmr with those reported (5). Structure **1** was also in accord with the ^{13}C -nmr spectrum (assignments on the structure), which was not previously given. This is only the second reported isolation of **1**, but the previous report (5) was also from the Lauraceae (*Cinnamomum triplinervis*). As far as we are

aware, no other natural compounds contain the methylsulfonylallyl moiety of **1**, although some *Allium* (onion) components have related structures.

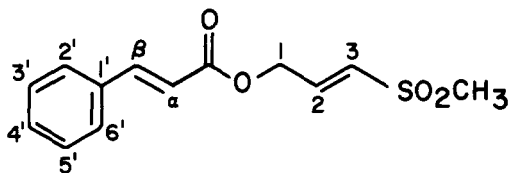
In the past, a number of species better belonging to *Phoebe* have been classified as *Cinnamomum*, although *Cinnamomum sensu strictu* is apparently never confused with *Phoebe* (6). The presence of **1** may be of value in a reexamination of the position of *C. triplinervis*.

EXPERIMENTAL

PLANT MATERIAL.—*P. mexicana* and *P. brenesii* were collected in Costa Rica and identified by L.J. Poveda A. of the Museo Nacional, San Jose, where voucher specimens are deposited.

EXTRACTION AND ISOLATION.—Stem bark (1 kg) of *P. mexicana* was extracted with EtOH, and the EtOH was evaporated to yield a residue that was suspended in H_2O -MeOH (4:1). The suspension was extracted with CHCl_3 and then EtOAc. The CHCl_3 extract yielded, after Si-gel chromatography, 100 mg of crude (+)-sesamin, which was recrystallized from EtOH to yield 50 mg, mp 120-121°, lit. (7) mp 122-123° and $[\alpha]_D +68^\circ$, lit. (7) $+68^\circ$. The EtOAc fraction, after Si-gel chromatography, yielded 150 mg of amorphous (-)-epicatechin, mp 223-224° dec., lit. (8) mp 242°, $[\alpha]_D -60^\circ$, lit. (7) -69° .

Stem bark (3.4 kg) of *P. brenesii* was extracted with petroleum ether and then EtOH. The EtOH

**1**

165.51 (C=O)	130.54 (C-4') ^a	116.41 (C- α)
146.13 (C- β)	130.01 (C-3')	61.35 (C-1)
141.22 (C-2)	128.79 (C-3', 5')	42.73 (S-CH ₃)
133.75 (C-1')	128.03 (C-2', 6')	

^aMay be interchanged.

residue after evaporation was partitioned between H₂O and Et₂O and the Et₂O evaporated. Recrystallization of the Et₂O residue from Et₂O-MeOH gave 7.5 g of crystalline **1**, mp 97-98°, lit. (5) mp 97-100°. Wood (1.2 kg) of *P. brenesii* was extracted with EtOH, concentrated, and the residue suspended in H₂O-MeOH (4:1). This was extracted with Et₂O and the Et₂O evaporated to yield a residue showing traces of **1**, along with 3.6 g of the major component, benzyl *trans*-cinnamate. The structure was proven by benzylation of *trans*-cinnamic acid chloride. Each species was examined as previously (1-3) for alkaloids, but none were found.

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