

ALKALOIDS OF *ALPHONSEA SCLEROCARPA*¹DRAGANA TADIĆ, G. PERCY WANNIGAMA,² BRUCE K. CASSELS, and ANDRÉ CAVÉ**Laboratoire de Pharmacognosie, UA 496 CNRS, Faculté de Pharmacie, 92296 Châtenay-Malabry, France*

The genus *Alphonsea* (Annonaceae) comprises about 30 species of small trees and shrubs growing in India, Sri Lanka, southeast Asia, and the Malaysian region (1). Of these, the only one that has been studied chemically is *Alphonsea ventricosa*, which contains glaucine, norglucine (2), and a large number of long-chain furanic diacetylenes (3). We now report the chemical examination of *Alphonsea sclerocarpa* Thw. from Sri Lanka.

The bark of this tree contained 0.036% of non-quaternary alkaloids of which liriodenine (12% of the crude bases), anonaine (5.5%), norushinsunine (5.0%), ushinsunine (4.5%), stepharine (2.0%), and stepholidine (7.0%) were identified. The bark also yielded a fairly large amount of quaternary bases (0.09% as the crude chlorides); only candicine (30%), phenethyltrimethylammonium (9.0%), and magnoflorine (4.7%) were characterized. The leaves gave 0.135% of non-quaternary alkaloids of which crotsparine was the main constituent (25%), accompanied by its rearrangement product sparsiflorine (4.0%), and lauroretanine (7.0%), isoboldine (5.5%) liriodenine (5.0%), and petalinemethine (4.0%).

Most of these alkaloids are frequent constituents of Annonaceae. The high candicine content of *A. sclerocarpa* is noteworthy as this appears to be the first time that this simple biogenetic derivative of tyrosine has been found in a member of this family. Phenethyltrimethylammonium ion is just as simply derivable from phenylalanine, and it is rather surprising that its only previous record as a natural product is as a constituent of the orchid *Eria jarensis* (4). Petalinemethine has only been isolated previously from *Leontice leontopetalum* (Berberidaceae) (5, 6) and is believed to be an artifact formed from the quaternary petaline, which is extremely sensitive to basic conditions (6). The unusual 7,8,4'-trioxygenation pattern of benzylisoquinolines like petaline has never been observed before in the Annonaceae.

EXPERIMENTAL

PLANT MATERIAL.—Trunk bark and leaves of *A. sclerocarpa* were collected by Prof. S. Balasubramaniam in the Wilpattu wild life sanctuary, Sri Lanka in May 1985. A voucher specimen is preserved in the Department of Botany, University of Peradeniya, Sri Lanka under number CH 378.

EXTRACTION AND ISOLATION.—The dried bark (1.1 kg) was defatted with petroleum ether, basified with 5% NH₄OH and percolated with CH₂Cl₂. The CH₂Cl₂ solution was concentrated and extracted with 10% citric acid followed by 5% H₃PO₄, and the combined acid solutions were basified with 10% NH₄OH and reextracted with CH₂Cl₂. Evaporation of the solvent afforded 400 mg of crude non-quaternary bases. These were chromatographed over Si gel, eluting with hexane-CH₂Cl₂-MeOH (33:66:2). The marc was exhausted with MeOH, the concentrated solution was treated with Mayer's reagent, and the precipitate collected, dissolved, and passed through an anion exchange column (C1⁻ form). The eluate was concentrated to dryness to yield 1.04 g of crude quaternary alkaloid chlorides. This mixture was chromatographed over a Si gel column, eluting with CH₂Cl₂-MeOH-NH₄OH (14:4:1). The dried leaves (400 g) were extracted in the same way as the bark, giving 540 mg of crude alkaloids which was chromatographed over Si gel, eluting with CH₂Cl₂ containing increasing concentrations of MeOH.

Details of the identification of the bases are available on request.

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FLAVONOIDS OF *COTULA CINEREA*

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Cotula L. (Compositae), the largest genus in the tribe Anthemideae (1), is a widespread Southern hemisphere group of about 80 species. The Anthemideae was arranged by Reitsebrecht (2) into seven provisional subtribal groups and follows the original scheme of Bentham (3). *Cotula* and its relatives are placed in the "Cotuleae" by Lloyd (1972) (4). Currently, the generic affinities of *Cotula* remain unclear, although the genus itself is adequately well defined (3). Previously (5) kaempferitin, quercetrin, quercetin, and kaempferol were reported from *Cotula cinerea* L.; we now describe different flavonoids from another population of this same species, namely: the 7-O- β -D-glucoside (6), 7-O- β -D-diglucoside, and 6-hydroxy-7-O- β -D-glucoside of luteolin (7), and luteolin itself, as well as apigenin 7-O- α -L-rhamnoside (8). These structures, along with the 6-C-arabinosyl-8-C-glucosylapigenin, isoschaftoside, are the primary flavonoid constituents of this species.

In addition, minor amounts of the 3-O- β -D-glucoside, 3-O- β -D-galactoside, and 7-O- β -D-glucoside of quercetin (9) as well as 5,3',4'-trihydroxy 3,6,7-trimethoxyflavone (10) were isolated.

Although 5-O-glycosylated flavonoids (11) usually distinguished *Cotula* from other members of the tribe Anthemideae, in our study no compounds with this substitution pattern were detected. However, glycosylated flavones such as those described here have been reported from other members of the tribe (1).

EXPERIMENTAL

PLANT MATERIAL.—Aerial parts of *C. cinerea* were collected 200 km north of Cairo on the Alexandria-Cairo desert road, Egypt in February 1985. The previously investigated population (5) was collected 67 km south of Cairo.

A voucher specimen (A. Ahmed #53), identified by Prof. Dr. El-Hadidi, Department of Botany, Cairo University, is deposited in the Herbarium of the Department of Botany, El-Minia University.

EXTRACTION, ISOLATION, AND IDENTIFICATION.—Dried, aerial parts of *C. cinerea* (500 g) were extracted twice each with 80% and 50% aqueous MeOH, and the concentrated syrup was chromatographed over a Polyclar AT column, eluted with H₂O, and then with increasing amounts of MeOH. The glycosides were further purified utilizing pc (Whatmann 3MM) with TBA (*t*-BuOH-HOAc-H₂O, 3:1:1), BAW (*n*-BuOH-HOAc-H₂O, 4:1:5 upper phase), and 15% HOAc as solvent systems. All compounds were purified over Sephadex LH-20 prior to spectral analysis by uv, ¹H nmr (as trimethylsilyl ethers in CCl₄), and ms. The glycosides were hydrolyzed to their respective aglycones and sugars, all of which were identified by authentic sample comparisons.

Details are available from the senior author.

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