FLAVONOIDS OF *LORANTHUS EUROPAEUS*[1]

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Mistletoes are semiparasitic plants that, in modern botanical taxonomy, are classified into two families: the Loranthaceae and Viscaceae (1). In a previous investigation (2), we found that *Viscum album* L. contained a number of methylated quercetin derivatives. No differences could be seen in the flavonoid pattern of *V. album* grown on different trees. This was also true for *Phoradendron tomentosum* (DC.) Gray (3). In the latter, we found apigenin C-glycosides (vitexin, schaftoside, and isoschaftoside) together with apigenin and apigenin 4′-O-glucoside. Crawford and Hawksworth (4) described myricetin and quercetin derivatives for different species of the genus *Arceuthobium*. Sakurai and Okumura (5) isolated different taxifolin derivatives of the Japanese mistletoe *Taxillus kaempferi* (DC.) Danser.

The present paper describes the characterization of three flavonoids of *Loranthus europaeus* L. The EtOAc fraction of a MeOH extract (see Experimental section) showed several spots on tlc that stained orange and greenish-yellow with NA-reagent (Naturstoffreagenz-A, Carl Roth, Germany), thus indicating that quercetin and kaempferol derivatives might be present. Purification of the extract by means of Craig distribution, droplet countercurrent chromatography (DCCC), and polyvinylpyrrolidone (PVP) chromatography yielded three flavonoid glycosides characterized by their uv and ^{1}H-nmr spectra, and tlc of the sugar after acid hydrolysis. A bathochromic shift of the long wave uv maxima after hydrolysis as well as chromatographic and pmr data of the glycosides revealed that the sugar was attached to the 3-position.

The ^{1}H-nmr data were in accordance with the kaempferol and quercetin skeletons. In each of the three compounds the 7-CH_3 group appeared at 3.9 ppm. The anomeric proton of the sugar appeared at 5.2 ppm for the 7-methyl kaempferol derivative, rhamnocitrin-3-*O*-rhamnoside and at 5.3 ppm and 5.5 ppm for the 7-methyl-quercetin derivatives, namely rhamnetin-3-*O*-glucoside and rhamnetin-3-*O*-rhamnoside, respectively.

The color reaction with NA-reagent indicates that additional flavonoid compounds of the kaempferol and quercetin types are present in minor amounts. Further research on the flavonoid chemistry of mistletoes will be necessary before these secondary compounds may prove useful as taxonomic markers.

EXPERIMENTAL

PLANT MATERIAL.—*L. europaeus* leaves were collected near Volos, Greece, from *Aesculus hippocastanum* host trees. A voucher specimen is deposited in the herbarium of the Botanical Institute of the University of Athens.

EXTRACTION AND ISOLATION.—Air-dried leaves (400 g) were coarsely powdered and allowed to macerate overnight with 2 liters of 80% MeOH on a rotary shaker. This procedure was repeated four times. The filtrates were combined and the MeOH evaporated under reduced pressure at 40°. The aqueous residue was partitioned between petroleum ether (50°-70°) (2×1 liter), $CHCl_3$ (2×1 liter) and EtOAc (4×1 liter). The EtOAc extract was dried over Na_2SO_4 and then evaporated. The residue was dissolved in a small amount of MeOH and fractionated through a Sephadex-LH-20-column with MeOH. The eluents were tested for flavonoids, and flavonoid containing fractions were combined.

These fractions were subjected to a Craig distribution with 70 steps in a two-phase system: $CHCl_3$-MeOH-*n*-PrOH-H_2O (10:10:1:6) using the upper phase as the mobile phase. The flavonoid-containing fractions were further cleaned by droplet counter DCCC (DCC A, Fa. Zinsser, Frankfurt) with the solvent system mentioned above for Craig distribution. Final separation was achieved on a PVP column with $CHCl_3$-MeOH-methylethylketone-M_2CO (20:10:5:1). All fractions from Sephadex, Craig, DCCC, and PVP chromatography were checked by tlc on cellulose plates with 15% HOAc, 40% HOAc, and *n*-BuOH-HOAc-H_2O (4:1:1), upper phase; spray reagent NA (0,1% in MeOH).

SPECTROSCOPY.—^{1}H-nmr spectra were run in DMSO-d_6 90 MHz. Uv spectra with shift reagents were run according to Mabry *et al.* (7).

HYDROLYSIS.—TFA (1 ml 0.1 N) and 1 mg flavonoid in a steam bath were heated for 30 min (6).

[1]This is part 3 of a communication of mistletoe flavonoids. For part 2, see Dossaji *et al.* (3).

Sugars and authentic reference samples were chromatographed on cellulose plates with pyridine-EtOAc-HOAc-H_2O (36:36:7:21). Spray reagent: aniline-phthalate (Merck).

ACKNOWLEDGMENTS

We thank Dr. R. Mues, Saarbrücken, for fruitful discussion.

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Received 9 March 1984

ALCALOÏDES DE *BONAFOUSIA MACROCALYX*[1]

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Le genre *Bonafousia* (Apocynacées, sous-tribu des Tabernae montaninées) (4) a été jusqu'ici peu étudié (5-8). La présente étude concerne une espèce de Guyane *Bonafousia macrocalyx* (Muell. Arg.) Boiteau et L. Allorge, dans les graines de laquelle avait déjà été signalée la présence de tabersonine et de coronaridine (7).

PARTIE EXPERIMENTALE

MATÉRIEL.—Les échantillons de *B. macrocalyx* ont été récoltés par l'un de nous à Saül, et dans la région du Haut Maroni. Des collections d'herbier sont déposées au Muséum National d'Histoire Naturelle de Paris et à l'herbier du Centre ORSTOM de Cayenne, Guyane française (réf. "Moretti 163", "Sastre et Moretti 3883").

EXTRACTION ET CARACTÉRISATION DES ALCALOÏDES.—Les spectres ont été enregistrés comme suit: uv, Unicam SP 1800; ir, Perkin-Elmer 257; rmn-^{1}H, Varian T60A et EM 390; rmn-^{13}C, Varian CFT 20, sm (EI et CI), Laboratoire central du CNRS, Lyon-Solaize. Toutes précisions expérimentales sont disponibles près des auteurs.

Ecorces de troncs.—L'extraction a été conduite de façon classique à partir d'un extrait méthanolique de poudre d'écorces (2300 g). La chromatographie des bases totales (35g) sur Kieselgel (solvants: C_6H_6, CH_2Cl_2, MeOH), puis une purification par clhp et ccm fournit la coronaridine, la voacangine, et l'heynéanine, la voacangarine (voacristine) (alcaloïde majoritaire), la voacangarine-hydroxy-7 indolénine, l'épi-19 voacangarine, la coronaridine-hydroxy-7 indolénine, la voacangine hydroxy-7 indolénine et l'oxo-3 coronaridine-hydroxy-7 indolénine, identifiées par comparaison avec des échantillons authentiques ou les données des publications (spectres ir, rmn ^{1}H et ^{13}C, sm). L'identité de l'oxo-3 coronaridine-hydroxy-7 indolénine a été confirmée par corrélation chimique avec la coronaridine (oxydation par l'iode) (9). Des contrôles ont montré que les hydroxy-indolénines isolées n'étaient pas des artéfacts d'extraction.

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[1]Cete étude a fait l'objet de communications préliminaires au Colloque "Substances nautrelles d'intérêt biologique" Nouméa, Août 1979 (1) et au 5è Colloque consacré aux Plantes Médicinales, Angers, Mai 1983 (2). Une publication partielle a, d'autre part, été consacrée à l'isolement de la voacangarine-hydroxy-indolénine et de l'acétate d'α-amyrine (3). Dans chaque cas, la plante était désignée sous le nom provisoire d'*Anacampta angulata* (Mart. ex Muell. Arg.) Miers.