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FLAVONOIDS OF *COTULA CINEREA*

AHMED A. AHMED,

Department of Chemistry, Faculty of Science, El-Minia University, El-Minia, Egypt

NABIL H. EL-SAYED, SABRY I. EL-NEGOUMY,

National Research Centre, Dokki, Cairo Egypt

and TOM J. MABRY*

The Department of Botany, The University of Texas, Austin, Texas 78713

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 Reitbrecht (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 H_2O, and then with increasing amounts of MeOH. The glycosides were further purified utilizing pc (Whatmann 3MM) with TBA (*t*-BuOH-HOAc-H_2O, 3:1:1), BAW (*n*-BuOH-HOAc-H_2O, 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, ^{1}H nmr (as trimethylsilyl ethers in CCl_4), 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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MICROBIAL TRANSFORMATION OF ZEARALENONE, I. FORMATION OF ZEARALENONE-4-*O*-β-GLUCOSIDE

SALEH EL-SHARKAWY[1] and YUSUF ABUL-HAJJ*

Department of Medicinal Chemistry and Pharmacognosy, College of Pharmacy, University of Minnesota, Minneapolis, Minnesota 55455

Zearalenone is a natural mycotoxin produced by a number of *Fusarium* species, particularly *F. roseum* (*graminearum*) and *F. tricinctum* (1-4). This compound has been associated with a hyperestrogenic syndrome causing serious problems when fed to many classes of livestock (6,7). The diseased animals show signs of genital disorders involving vulvovaginitis, edematous uterus, and overian atrophy (7). In addition, it was reported (5-9) that zearalenone and some of its derivatives have anabolic effects and are currently used as growth promoters. The screening of 150 microorganisms for transformation of zearalenone showed several metabolites including α- and β-zearalenone, and β-zearalanol. The present communication describes studies related to the bioconversion of zearalenone to zearalenone glucoside by *Thamnidium elegans* and *Mucor bainieri*.

Small-scale experiments with 150 fungi showed that only two cultures produced a unique metabolite that had a low Rf value that was obtained in considerable yields by *T. elegans* (60%) and *M. baineiri* (30%). Large-scale fermentations with *T. elegans* were carried out to obtain sufficient quantities of the metabolite for structure elucidation. The metabolite was identified as zearalenone-4-*O*-β-glucoside on the basis of ir, nmr, and mass spectral analysis.

After this report was submitted for publication, Kamimura (10) reported the structure of zearalenone-4-*O*-β-glucoside produced through microbial conversion of zearalenone by a species of *Rhizopus*, and the spectral data supporting the structure can be found in that reference.

EXPERIMENTAL

Melting points were determined on a Fisher-Jones hot plate apparatus and are uncorrected. Ir spectra were taken with a Perkin-Elmer 281 spectrophotometer using nujol discs. High resolution mass spectra were determined on an LKB 9000 GC mass spectrometer. Nmr were taken in $CDCl_3$ or acetone-d_6 using TMS as an internal standard. ^1H nmr and C^{13} nmr were taken on a 300 MHz Nicolet NT-300-W3 spectrometer.

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