FLAVONOIDS FROM *HAPLOPAPPUS FOLIOSUS*

AYHAN ULUBELEN and ESER AYANOGLU

Faculty of Pharmacy, University of Istanbul, Istanbul, Turkey

and

W. DENNIS CLARK and GREGORY K. BROWN

Department of Botany and Microbiology, Arizona State University, Tempe, Arizona

and

TOM J. MABRY

Department of Botany, University of Texas at Austin, Austin, Texas

We have previously reported *Haplopappus* flavonoids from *H. canescens* (1) of section *Haplopappus*, *H. integerrimus* var. *punctatus* (2) of section *Steriphe*, and *H. rengifoanus* (3) of section *Polyphylla*. Species of *Polyphylla* are more similar morphologically to related North American species of the genus *Hazardia* (4), whose flavonoid chemistry is already known (5). We report here further investigations of the flavonoids of *Haplopappus* section *Polyphylla* as a basis for chemotaxonomic comparisons between it and *Hazardia*.

EXPERIMENTAL[1]

PLANT MATERIAL.—Collections of *H. foliosus* DC. leaves were made in Prov. Coquimbo, Chile, 2 km south of Los Vilos (Clark and Brown 1323) and at the northern edge of Pichidangui (Clark and Brown 1327) in January, 1979. Voucher specimens are deposited in the herbarium at Arizona State University.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—All of the general chromatographic techniques employed were described in the previous report on the flavonoids of *Haplopappus rengifoanus* (3). Dried and powdered leaves of collection No. 1327 (250 g) and No. 1323 (400 g) were separately extracted with aqueous ethanol (85%). The extracts were concentrated *in vacuo* to aqueous syrups; these concentrates were extracted successively with petroleum ether (bp 30–60°), chloroform, and ethyl acetate. Most of the flavonoids from No. 1327 remained in the aqueous fraction, while those of No. 1323 were found in the chloroform and ethyl acetate fractions, which were therefore combined.

A Polyclar column (4.5 x 50 cm) was used for the separation of 10 g of the phenolic concentrate from the extract of No. 1327. Elution was initiated with ethanol, the polarity of which was increased by the gradual addition of water up to 100%. Elution of the Polyclar column (3 x 40 cm) used for 5 g of the phenolic concentrate of the chloroform-ethyl acetate extracts from the work-up of No. 1323 was initiated with Egger's solvent, the polarity of which was increased by gradually reducing the amount of chloroform.

KAEMPFEROL 3-METHYL ETHER 7-β-D-GLUCOSIDE (10 mg).—Although the 7-rutinoside of kaempferol 3-methyl ether is known from another member of the Compositae, namely *Centaurea arguta* (6), it appears that the 7-glucoside has not been previously reported. β-Glucosidase and acid hydrolysis (0.1 N TFA) of this new glycoside yielded kaempferol 3-methyl ether (uv, pmr, ms, and tlc comparison with a standard sample) and glucose. A shoulder at 410 nm with NaOAc relative to Band I in the NaOMe spectrum (390 nm) and no Band III (7), as well as no shift in Band II relative to Band II in the MeOH spectrum (270 nm) indicated that the 7-OH was substituted. Pmr showed one methyl signal at δ 3.84, signals for an apigenin-type B ring and doublets (J=2.5 Hz) for H-6, H-8. Complete uv and ms data are: uv λ max (MeOH) 350, 300 (sh), 270; NaOMe, 390 (higher intensity), 270; $AlCl_3$, 400, 350, 302, 275; $AlCl_3$/HCl, 396, 344, 300, 272; NaOAc, 410 (sh), 356, 294, 268; NaOAc/H_3BO_3, 348, 295, 264; ms (underivatized), M^+ agly., 300 (100); (M+1), 301 (30); (M–1), 299 (80); (M–H_2O), 282 (25); (M–CO–CH_3), 257 (40); (A+1), 153 (27); B_2, 121 (55).

QUERCETIN 3-β-D-GLUCOSIDE (12 mg) and 3-β-D-GALACTOSIDE (11 mg), ISORHAMNETIN 3-β-D-GLUCOSIDE (9 mg), AND KAEMPFEROL 3-β-D-GLUCOSIDE (10 mg).—Each of the compounds yielded the expected algycones and sugars when hydrolyzed with both enzymes and acid (0.1 N TFA). The pmr and uv spectral data, colors under uv before and after hydrolysis, and direct tlc comparison with authentic samples established their structures.

ISORHAMNETIN (8 mg), QUERCETIN 3-METHYL ETHER (15 mg), KAEMPFEROL (10 mg), KAEMPFEROL 3-METHYL ETHER (16 mg), AND ESCULETIN (20 mg).—Uv, pmr, ms, and direct tlc comparison with standard samples

[1]Spectra were recorded with the following instruments: uv Varian Techtron Model 635; pmr Varian 90 MHz and Varian 200 MHz; ms DuPont 21-491. Adsorbents for cc and tlc were from E. Merck and Macharey-Nagel.

established the identities of these compounds.

EUPATOLITIN (3 mg).—Uv and ms spectral properties and color reactions under uv light (366 nm), with uv and NH_3 (yellow), and when sprayed with NA reagent (orange) showed that this compound was quercetagetin 6,7-dimethyl ether (eupatolitin) (8).

ACKNOWLEDGMENTS

The work at Arizona State University was supported by the National Science Foundation (Grant No. DEB-7823897), at the University of Texas by the Robert A. Welch Foundation (Grant No. F-130), and at the University of Istanbul by the Faculty of Pharmacy.

Received 10 October 1980

LITERATURE CITED

1. S. Oksuz, A. Ulubelen, W. D. Clark, G. K. Brown and T. J. Mabry, *Rev. Latinoamer. Quim.*, **12**, 12 (1981).
2. E. Ayanoglu, A. Ulubelen, W. D. Clark, G. K. Brown, R. R. Kerr and T. J. Mabry, *Phytochemistry*, **20**, 1715 (1981).
3. A. Ulubelen, W. D. Clark, G. K. Brown and T. J. Mabry, *J. Nat. Prod.*, **44**, 294 (1981).
4. W. D. Clark, *Madroño*, **26**, 105 (1979).
5. W. D. Clark and T. J. Mabry, *Biochemical Systematics and Ecology*, **6**, 19 (1978).
6. J. L. Breton, A. G. Gonzalez and S. O. Ruiz, *An. Real Soc. Espan. Fis. Quim.*, **63**, 703 (1967).
7. J. D. Bacon and T. J. Mabry, *Rev. Latinoamer. Quim.*, **7**, 83 (1976).
8. L. Quijano, F. Malanco and T. Rios, *Tetrahedron*, **26**, 285 (1970).