

FLAVONOIDS OF *BACCHARIS INCARUM*

FRANCESCA A. FAINI and MARIANO CASTILLO

*Departamento de Química, Facultad de Ciencias Básicas y Farmacéuticas,
Universidad de Chile, Las Palmeras 3425, Santiago*

M. RENÉ TORRES

*Departamento de Química, Facultad de Ciencia, Universidad de Santiago de Chile,
Ecuador 3469, Santiago*

Baccharis (Astereae), one of the genera of the Compositae, comprises about 400 species restricted to the American continent (1). About 36 species have been described in Chile. Relatively few members of this genus have been studied chemically and, so far, the results do not present a clear picture (2). In connection with our work on terpenoids of *Baccharis* (3), we have undertaken a search of

flavone was isolated for the first time as a natural product from *Citrus sudachi* and identified as 7-methylsudachitin by direct comparison with the synthetic compound (8). Lack of authentic samples and the limited spectroscopic information available led us to examine the ^{13}C -nmr spectra and perform NOE experiments in order to confirm the proposed structures (tables 1 and 2).

TABLE 1. ^1H nmr data of 1 and 2.

	1	2
H-3.....	—	6.60 (s)
H-2'.....	7.80 (d,1.9)	7.41 (d,2.1)
H-5'.....	7.07 (d, 7.07)	7.06 (d, 8.6)
H-6'.....	7.79 (dd, 8.9,1.9)	7.54 (dd, 8.6,2.1)
5-OH.....	12.4 (s)	12.56 (s)
4'-OH.....	6.08 (bs)	6.16 (bs)
3'-OMe.....	3.88 (s) ^b	4.01 ^b
	3.96 (s,6H)	3.96 (s,3H)
	3.99 (s,3H)	3.98 (s,3H)
	4.11 (s,3H)	4.12 (s,3H)

^aIn CDCl_3 , ppm from TMS (J values in Hz).

^bAssigned by NOE: 20% increase of intensity of H-2' signal.

flavonoids to determine if the chemistry may give indications of the relationships in this diverse group. One of the species studied, *Baccharis incarum* Wedd, afforded two flavones of very rare natural occurrence.

The first flavone corresponded to 5,4'-dihydroxy-3,6,7,8,3'-pentamethoxyflavone (1), isolated for the first time from *Calycopteris floribunda* (4) and later on from *Digitalis thapsi* (5). The other flavone, 5,4'-dihydroxy-6,7,8,3'-tetramethoxyflavone (2), corresponded to a synthetic product prepared by Wagner (6), who thus showed that its purported occurrence in *Deuterophoma tracheiphila* was erroneous (7). Very recently, this

TABLE 2. ^{13}C nmr data of 1 and 2^a.

	1	2
C-2.....	156.1	174.0
C-3.....	138.9	104.0
C-4.....	179.5	183.0
C-5.....	153.1	153.2
C-6.....	133.1	131.0
C-7.....	146.8	147.3
C-8.....	123.1	126.3
C-9.....	145.1	145.9
C-10.....	107.7	107.2
C-1'.....	122.8	121.0
C-2'.....	111.2	108.0
C-3'.....	148.9	149.8
C-4'.....	149.4	149.7
C-5'.....	115.0	115.0
C-6'.....	123.1	121.0

^aIn CDCl_3 , ppm from TMS. The assignments were based on SFORD techniques and by comparison with literature data.

These results bring to 15 the number of species of *Baccharis* examined for flavonoids. On examination of the data accumulated so far, one can distinguish three groups which may be of chemosystematic interest. The first comprises species which only accumulate flavones (including 3-methoxylated flavones): *B. crispa*, *B. sarothroides*, *B. rhomboidalis*, *B. tricuneata* v. *tricuneata*, *B. trimera* and *B. incarum*. The second group comprises species which only accumulate flavanones: *B. intermixta*, *B. varians*, *B. serrulata*, *B. reticularia*, *B. salzmännii*, *B. alaternoides*, *B. sclicifolia*, *B. retusa*. The third group, comprising only one species, shows flavonol glycosides: *B. angustifolia*. In this respect, it is of interest to mention the observation made by Bohlman indicating that species which accumulate flavanones often co-occur with baccharis oxide (9-16). Additional chemical studies of this group of secondary metabolites may shed further light on these relationships.

EXPERIMENTAL¹

PLANT MATERIAL.—*Baccharis incarum* Wedd, collected in Toconce (Antofagasta) in February, 1980, was identified by C. Marticorena (University of Concepción). A voucher specimen is deposited in the U.C. Herbarium.

EXTRACTION AND ISOLATION OF THE FLAVONOIDS.—Dried and powdered leaves (1.5 kg) were extracted with petroleum ether (3 liters) followed by methanol (3 liters). The chilled concentrated methanol extract yielded a copious precipitate (7.5 g) consisting mainly of oleanolic acid. The mother liquors were concentrated *in vacuo*, diluted with water and further extracted with ethyl ether and chloroform. The organic solutions, when evaporated to dryness, yielded 26.5 and 3.2 g of residue, respectively. Examination of both fractions (tlc, Si gel, chloroform-methanol, 95:5) showed the presence of two flavonoids. The ethyl ether residue (4.5 g) were chromatographed on a Si gel column with chloroform-methanol in increasingly polar ratios.

5,4'-DIHYDROXY-3,6,7,8,3'-PENTAMETHOXYFLAVONE (3-METHOXYCALICOPTERIN) (1). Yellow crystals (147 mg), mp 165-167° (MeOH), (Lit. 160-162°); ν_{\max} (MeOH) nm; 260, 278, 351; +NaOMe: 270, 297 (sh); +AlCl₃: 274, 284, 305 (sh), 377 and 405 (sh); +AlCl₃/HCl: 269, 288, 308 (sh), 370 and

405; +NaOAc: 269, 422; +NaOAc/H₃BO₃: 259, 275 and 353; high resolution mass spectrum, m/z (relative intensity): 404.1099 (M⁺, 60; C₂₀H₂₀O₈ requires 404.1107), 389.0855 (100, M⁺-15; C₁₉H₁₇O₈ requires 389.0873), 211.0231 (15; C₉H₇O₆ requires 211.0243), 183.0286 (12; C₈H₇O₅ requires 183.0294), 151.0391 (13; C₈H₇O₅ requires 151.0395).

5,4'-DIHYDROXY-6,7,8,3'-TETRAMETHOXYFLAVONE (7-METHYLSUDACHITIN) (2).—Yellow crystals (105 mg), mp 157-160° (MeOH) (Lit. mp. 160-161°); ν_{\max} (MeOH): 254, 281 and 344 nm; +NaOMe: 266, 292 (sh), and 411; +AlCl₃: 265, 286, 299 (sh) and 372; +AlCl₃/HCl: 262, 289, 296 (sh), 363 and 393 (sh); +NaOAc: 265, 290 and 412; +NaOAc/H₃BO₃: 278, 345; high resolution mass spectrum, m/z (relative intensity): 374.0986 (M⁺, 49; C₁₉H₁₈O₈ requires 374.1002), 359.0768 (100, M⁺ -15; C₁₈H₁₅O₈ requires 359.0767), 211.0245 (27; C₉H₇O₆ requires 211.0243), 183.0284 (19; C₈H₇O₅ requires 183.0294), 151.0390 (8; C₈H₇O₅ requires 151.0395).

ACKNOWLEDGMENTS

This study was supported by the S.D. C.A.C.I. (Universidad de Chile, grant Q-627 791) and the DICYT, DIPLAN II (Universidad de Santiago de Chile).

Received 26 October 1981

LITERATURE CITED

1. C. Reiche, "Flora de Chile—Volume IV", Cervantes, Santiago, 1905.
2. a) R. Hegnauer, "Chemotaxonomie der Pflanzen", band, 3, Birkhauser Verlag, Basel, 1964, p. 447.
b) F. Bohlmann, C. Zdero, M. Grenz, A. K. Dhar, H. Robinson and R. M. King, *Phytochemistry*, **20**, 281 (1981).
3. A. San Martín, J. Roviroso, V. Gambaro and M. Castillo, *Phytochemistry*, **19**, 1985 (1980).
4. A. V. Rama Rao and M. Varadan, *Indian J. Chem.*, **11**, 403 (1973).
5. J. de Pascual, F. Díaz, F. S. Sánchez, J. M. Hernandez and M. Grande, *Planta Medica*, **38**, 271 (1980).
6. H. Wagner, G. Mauer, L. Hörhammer, and L. Farkas, *Chem. Ber.*, **104**, 3357 (1971).
7. J. Pinkas, D. Lavie and M. Chopin, *Phytochemistry*, **7**, 169 (1968).
8. T. Horie and M. Nakayama, *Phytochemistry*, **20**, 377 (1981).
9. A. L. Bandoni, J. E. Medina, R. V. D. Rondina and J. D. Coussio, *Planta Medica*, **34**, 328 (1978).
10. S. Morris Kupchan and E. Bauer-schmidt, *Phytochemistry*, **10**, 664 (1971).
11. M. Silva and J. M. Mundaca and P. G. Sammes, *Phytochemistry*, **10**, 1942 (1971).
12. F. Bohlmann, W. Knauf, R. M. King and H. Robinson, *Phytochemistry*, **18**, 1011 (1979).
13. W. Herz, A. M. Piliotti, A. M. Söderholm, I. K. Shuhama and W. Vichnewski, *J. Org. Chem.*, **42**, 3913 (1977).
14. F. Bohlmann, C. Zdero, M. Grenz, A. K. Dhar, H. Robinson and R. M. King, *Phytochemistry*, **20**, 281 (1981).
15. J. Kavka, E. Guerreiro y O. S. Giordano y J. Romo, *Rev. Latinoameric. Quim.*, **4**, 101 (1973).
16. H. Wagner and M. A. Iyengar and W. Herz, *Phytochemistry*, **11**, 444 (1972).

¹ ¹H-nmr spectra were determined on a Bruker WH 200 spectrometer (200 MHz), and ¹³C-nmr spectra were determined on a Bruker WH 200 spectrometer (50 MHz); uv were recorded on a Varian Cary 17; ms on a Varian Mat 312.