

## NAPHTHOQUINONE CONSTITUENTS OF *TABEBUIA* SPP.

MICHEL GIRARD,\* D'ARYL KINDACK, BRIAN A. DAWSON,  
 JEAN-CLAUDE ETHIER, DENNIS V.C. AWANG,

Bureau of Drug Research, Health and Welfare Canada, Tunney's Pasture, Ottawa, Ontario K1A 0L2, Canada

and ALWYN H. GENTRY

Missouri Botanical Garden, St. Louis, Missouri 63161

As part of chemotaxonomic studies directed toward identification of commercial herbal products sold as Taheebo/Pau d'Arco/Lapacho/Ipe roxo, we have examined the naphthoquinone constituents of bark extracts from *Tabebuia* spp. (Bignoniaceae). Up until now, very little chemical work has been done specifically on bark because it is widely assumed that the naphthoquinone profile is similar in wood and bark for most species (1). Examination of fresh bark extract of *Tabebuia rosea* (Bertol.) DC. collected at Cartagena, Colombia, revealed that, unlike wood extract where mainly lapachol and dehydro- $\alpha$ -lapachone are found, bioactive naphthoquinones 2-acetyl-naphtho-[2,3-*b*]furan-4,9-dione, 2-(1-hydroxyethyl)-naphtho-[2,3-*b*]furan-4,9-dione and 5(or 8)-hydroxy-2-(1-hydroxyethyl)-naphtho[2,3-*b*]furan-4,9-dione are the major naphthoquinone constituents (Table 1). These three lapachol derivatives have been reported previously from *Tabebuia cassioides* (2) and were shown to be active against KB cells. Only traces of lapachol

and dehydro- $\alpha$ -lapachone were detected in that extract.

Bark extracts from two other species, namely, *Tabebuia impetiginosa* (Mart.) ex DC. (Standl.) and *Tabebuia chrysantha* (Jacq.) Nichols ("Tahuari"), also obtained from South America, showed similar profiles.

### EXPERIMENTAL

PLANT MATERIAL.—A sample of *T. rosea* was obtained from Cartagena, Colombia, in May 1987; a sample of *T. chrysantha* was collected in Peru in March 1987; a sample of *T. impetiginosa* was obtained from Peru in 1983. Voucher specimens are deposited at the Missouri Botanical Garden.

EXTRACTION AND ISOLATION.—Air-dried material was ground to a fine powder and extracted in a Soxhlet apparatus with petroleum ether (30–60°) for 48 h. An aliquot was withdrawn and evaporated to dryness at room temperature under reduced pressure. The residue was dissolved in a known volume of mobile phase and analyzed by hplc using the standard conditions reported earlier (3). The same aliquot was used for gc-ms analysis using the operating conditions described previously (4).

The bulk of the extract from *T. rosea* was concentrated using a rotary evaporator and extracted

TABLE 1. Naphthoquinones in Extracts from Various *Tabebuia* spp.

Compound	Extract			
	<i>Tabebuia rosea</i> (wood)	<i>T. rosea</i> (bark)	<i>Tabebuia impetiginosa</i> (bark)	<i>Tabebuia chrysantha</i> (bark)
Lapachol . . . . .	++ <sup>a</sup>	tr <sup>b</sup>	—	—
Dehydro- $\alpha$ -lapachone . . . . .	++	tr	—	—
2-Acetyl-naphtho[2,3- <i>b</i> ]- furan-4,9-dione . . . . .	—	+	+	+
2-(1-Hydroxyethyl)-naphtho- [2,3- <i>b</i> ]furan-4,9-dione . . . . .	—	++	+	+
5(or 8)-Hydroxy-2-(1-hydroxy- ethyl)-naphtho[2,3- <i>b</i> ]furan- 4,9-dione . . . . .	—	++	—	—

<sup>a</sup>0.003% (lapachol).

<sup>b</sup>< 0.0003% (lapachol).

with 2 N Na<sub>2</sub>CO<sub>3</sub>. The base-soluble fraction was recovered after acidification of the aqueous layer and extraction with Et<sub>2</sub>O. Isolation of the individual components from base-soluble and base-insoluble fractions was accomplished by preparative reversed-phase hplc eluting with MeCN-H<sub>2</sub>O (1:1). 5(or 8)-Hydroxy-2-(1-hydroxyethyl)-naphtho[2,3-*b*]furan-4,9-dione, 2-(1-hydroxyethyl)-naphtho[2,3-*b*]furan-4,9-dione and 2-acetyl-naphtho[2,3-*b*]furan-4,9-dione were obtained and identified from their respective <sup>1</sup>H nmr, ir, uv, gc-ms, and mp data and by comparison with values reported by Rao and Kingston (2). The structures of the latter two compounds were confirmed by comparison with authentic samples prepared from 2-isopropyl-naphtho[2,3-*b*]furan-4,9-dione (5).

Full details of extraction, identification, and

syntheses of these compounds are available upon request.

#### LITERATURE CITED

1. V.E. Tyler, L.R. Brady, and J.E. Robbers, "Pharmacognosy," 9th ed., Lea & Febiger, Philadelphia, 1988, p. 483.
2. M.M. Rao and D.G.I. Kingston, *J. Nat. Prod.*, **45**, 600 (1982).
3. D.V.C. Awang, D. Kindack, and B.A. Dawson, *J. Chromatogr.*, **368**, 439 (1986).
4. M. Girard, J.-C. Ethier, D. Kindack, B.A. Dawson, and D.V.C. Awang, *J. Nat. Prod.*, **50**, 1149 (1987).
5. A.V. Pinto, M. do C.R. Pinto, M.A. Aguiar, and R.S. Capella, *An. Acad. Bras. Cienc.*, **54**, 115 (1982).

Received 15 April 1988

#### Continued from back cover

A New Glycoside of 3-Nitropropanol from <i>Astragalus miser</i> var. <i>serotinus</i> —W. Majak, M.H. Benn, and Y.Y. Huang	985
Starfish Saponins, Part 35. Two Novel Steroidal Xyloside Sulfates from the Starfish <i>Marrhasterias glacialis</i> —Raffaele Riccio, Olinda Squillace Greco, and Luigi Minale	989
Ajugasterone C and 5-Deoxykaladasterone, an Ecdysteroid Artifact, from <i>Leuzea carthamoides</i> —K. Szendrei, E. Varga, Zs. Hajdú, I. Herke, R. Lafont, and J.-P. Girault	993
Chemistry of <i>Hyptis mutabilis</i> : New Pentacyclic Triterpenoids—Rogelio Pereda-Miranda and Mariano Gascón-Figueroa	996
3β,5α-Dihydroxy-6β-Methoxycholest-7-enes from the Marine Sponge <i>Spongia agaricina</i> —Anna Aiello, Patrizia Ciminiello, Ernesto Pastoruzzo, and Silvana Magno	999
Starfish Saponins, Part 36. Steroidal Oligoglycosides from the Pacific Starfish <i>Thromidia casalai</i> —Raffaele Riccio, Olinda Squillace Greco, Luigi Minale, Stéphane La Barre, and Dominique Laurent	1003
Structure of Cyperanic Acid, a New Sesquiterpene from <i>Dittrichia viscosa</i> —Paolo Ceccherelli, Massimo Curini, Maria Carla Marcotullio, and Alessandro Menghini	1006
Occurrence of Olepupane in Two Mediterranean Nudibranchs: A Protected Form of Polygodial—G. Cimino, G. Sodano, and A. Spinella	1010
Isolation of Dehydromoskachen C from <i>Ruta chalepensis</i> var. <i>lasifolia</i> —Ayban Ulubelen and Hüseyin Güner	1012
Chemistry of Sponges, V. Dicyodendrillolide, a New Prenylated Butenolide from a Sponge—R.C. Cambie, Patricia R. Bergquist, and P. Karuso	1014
Two New Dragendorff-Positive Compounds from Marine Algae—Sebastiano Sciuto, Rosa Chillemi, Raffaele Morrone, Angela Patti, and Mario Piattelli	1017
In Vitro Study of the Anticholinergic and Antihistaminic Activities of Protopine and Some Derivatives—Levent Üstünes, Geri M. Laekeman, Belkis Gözler, Arnold J. Vlietinck, Azli Özer, and Arnold G. Herman	1021
Naphthoquinone Constituents of <i>Tabebuia</i> spp.—Michel Girard, Daryl Kindack, Brian A. Dawson, Jean-Claude Ethier, Dennis V.C. Awang, and Alwyn H. Gentry	1023
Awards and Grants	900
Research Achievement Award	914