Journal of Natural Products
Vol. 47, No. 1, pp. 179-181, Jan-Feb 1984

CONSTITUENTS OF *PTEROCARPUS MARSUPIUM*

R. MAURYA, A.B. RAY,

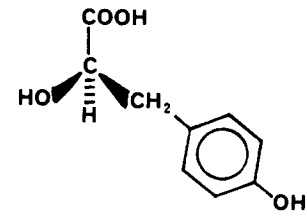
Department of Medicinal Chemistry, Institute of Medical Sciences, Banaras Hindu University, Varanasi-221005, India

F.K. DUAH, D.J. SLATKIN, and P.L. SCHIFF, JR.*

Department of Pharmacognosy, School of Pharmacy, University of Pittsburgh, Pittsburgh, PA 15261

Pterocarpus marsupium Roxb. (Leguminosae), also known as Indian Kino or Bija Sar, is a large tree common to the mixed deciduous forests of central and peninsular India (1). Extracts of the leaves, flowers, and gum of this tree have been used medicinally in the treatment of diarrhea, toothache, fever, and urinary tract and skin infections (1,2), while extracts of the bark or heartwood have been controversially regarded as useful in the therapy of diabetes (1-13). Previous research has established the genus *Pterocarpus* to be a rich source of polyphenolic compounds (14), and extracts of *P. marsupium* have afforded the stilbene, pterostilbene (15,16); the catechin, epicatechin (8); the flavonoids pseudobaptigenin, liquiritigenin, garbanzol, and 5-deoxykaempferol (17); the chalcone, isoliquiritigenin (17); the dihydrochalcone, pterosupin (17); the isoflavonoid glycol, marsupol (4,4′-dihydroxy-α-methylhydrobenzoin) (18); and the aromatic aldehyde, p-hydroxybenzaldehyde (17). In addition, the sesquiterpene alcohols, β-eudesmol (16), selin-4(15)-en-1β,11-diol(16) and pterocarpols A and B (19), and the triterpene alcohol erythrodiol-3-monoacetate (16) have been isolated from this species.

We report here the isolation and identification of phenolic compounds from an extract of the heartwood of *P. marsupium*. The dried, powdered heartwood of *P. marsupium* was defatted with petroleum ether and subsequently extracted with EtOAc. The EtOAc extract was concentrated and chromatographed over silica gel in C_6H_6. Elution with C_6H_6 initially afforded pterostilbene, followed by (2*S*)-7-hydroxyflavanone, the latter of which has been previously isolated from species of the genera *Flemingia* (Leguminosae) and *Platymiscium* (Leguminosae) (20). To our knowledge, this is the first reported isolation of this simple flavanone from the genus *Pterocarpus*. Elution with C_6H_6-EtOAc (19:1) afforded isoliquiritigenin and liquiritigenin, while elution with C_6H_6-EtOAc (9:1) gave 7,4′dihydroxyflavone and 5-deoxykaempferol (3,7,4′-trihydroxyflavone). 7,4′Dihydroxyflavone has been previously isolated from the legumes *Trifolium repens*, *Medicago sativa*, *Castanospermum australe*, and *Sophora* species (21), but this appears to be the first reported isolation of this flavone from the genus *Pterocarpus*. Elution with C_6H_6-EtOAc (3:1) afforded the benzofuranone marsupsin, whose structural determination has been described previously (22), and an incompletely characterized phenol designated PM-33. Elution with C_6H_6-EtOAc (1:3) yielded the glucosidic-β-hydroxydihydrochalcone pterosupin. Finally, the EtOAc eluent was rechromatographed over silica gel, and elution with C_6H_6-Me_2CO (9:1) gave *p*-hydroxybenzaldelyde while elution with C_6H_6-Me_2CO (4:1) afforded (2*R*)-3-(*p*-hydroxyphenyl)-lactic acid (**1**). Although p-



1

hydroxyphenyllacetic acid (stereochemistry unspecified) has been isolated from rice-koji in the Japanese brewing industry (23), to our knowledge this is the first reported isolation of (2*R*)-3-(p-hydroxyphenyl)-lactic acid from the genus *Pterocarpus* or from the family Leguminosae.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were taken on a Fisher-Johns Apparatus and are uncorrected. The uv spectra were obtained on a Perkin-Elmer model 202 recording spectrophotometer in MeOH, and the ir spectra were determined on a Perkin-Elmer model 257 recording spectrophotometer in $CHCl_3$ or KBr pellets. The ^{1}H-nmr spectra were recorded in $CDCl_3$ or deuterated MeOH on a Hitachi Perkin-Elmer model R-24 high resolution spectrometer with TMS as internal standard and chemical shifts recorded in δ (ppm) units. The mass spectra were taken with a Finnigan EI Mass Spectrometer interfaced with a Finnigan Incoj Data System, Extranuclear Laboratories, Inc.

PLANT MATERIAL.—The plant used in this study was collected in Varanasi, India, in 1979 and identified by Dr. R.L. Khosa, Division of Pharmacognosy of the Department of Pharmaceutics, Banaras Hindu University. A herbarium specimen is preserved in the Department of Medicinal Chemistry, Banaras Hindu University.

EXTRACTION AND FRACTIONATION.—Powdered, dried heartwood (2.4 kg) of *Pterocarpus marsupium* Roxb. was initially defatted by extraction with petroleum ether (60-80°) (10 liters) (Soxhlet) and subsequently extracted with EtOAc (10 liters) (Soxhlet). The EtOAc extract was dried (anhydrous Na_2SO_4), filtered, and the filtrate concentrated to a residue (60 g) that was dissolved in minimum volume of MeOH, adsorbed on silica (60 g), and freed from solvent in a vacuum desiccator. The adsorbed material was placed on a prepacked column of silica (300 g) in C_6H_6 (column A).

ISOLATION OF PTEROSTILBENE.—Elution of the column with C_6H_6 (3 liters) afforded pterostilbene (5 g), mp 84° (petroleum-$CHCl_3$), identical by direct comparison (mp, uv, ir, ^{1}H-nmr, ms) (16) and preparation of the *O*-methylether, mp 56°, and the *O*-acetylester, mp 123°, by standard procedures.

ISOLATION OF (2S)-7-HYDROXYFLAVANONE.—Further elution with C_6H_6 (600 ml) gave 7-hydroxyflavanone (15 mg), mp 192-193° (C_6H_6); $[\alpha]^{27}D$ −16° (c 0.19, MeOH); identical by direct comparison (mp, uv, ir, ms) with authentic spectra (24).

ISOLATION OF ISOLIQUIRITIGENIN.—Elution with C_6H_6-EtOAc (19:1) (700 ml) afforded isoliquiritigenin (110 mg), mp 209-210° (C_6H_6-EtOAc), identical by direct comparison (mp, uv, ir, ^{1}H-nmr, ms) with authentic samples (25).

ISOLATION OF LIQUIRITIGENIN.—Continued elution with C_6H_6-EtOAc (19:1) (700 ml) yielded liquiritigenin (125 mg), mp 203° (C_6H_6-EtOAc); $[\alpha]^{26}D$ −13° (c 0.2, MeOH), identical by direct comparison (mp, uv, ir, ^{1}H-nmr, ms) with authentic spectra (25).

ISOLATION OF 7,4'-DIHYDROXYFLAVONE.—Elution with C_6H_6-EtOAc (9:1) (600 ml) gave 7,4'dihydroxyflavone (53 mg), mp 165-166° (C_6H_6-EtOAc); identical by direct comparison (mp, uv) with authentic spectra (25) and preparation of the diacetate ester (Ac_2O+NaOAc), mp 187-189°.

ISOLATION OF MARSUPSIN.—Elution with C_6H_6-EtOAc (3:1) (900 ml) yielded marsupsin (135 mg), mp 193-195° (C_6H_6-EtOAc), $[\alpha]^{26}D$ −4° (c 0.5, MeOH), whose structural elucidation was previously described (22).

ISOLATION OF PM-33.—Continued elution with C_6H_6-EtOAc (3:1) (900 ml) gave PM-33 (35 mg), mp 314-315°, whose structure is currently undetermined.

ISOLATION OF PTERPSUPIN.—Elution with C_6H_6-EtOAc (1:3) (3 liters) afforded pterosupin (24 mg), mp 165-167° (C_6H_6-EtOAc); $[\alpha]^{26}D$ +51° (c 0.21, MeOH), identical by direct comparison (mp, uv, ir, ^{1}H-nmr) with authentic spectra (17) and sample (co-tlc).

ISOLATION OF P-HYDROXYBENZALDEHYDE.—Elution of the column with EtOAc (600 ml) afforded a residue (0.5 g) that was rechromatographed over silica (10 g) (column B). Elution with C_6H_6-Me_2CO (9:1) (100 ml) yielded *p*-hydroxybenzaldehyde (28 mg), mp 111° (C_6H_6-Me_2CO); identical by direct comparison (uv, ir, ^{1}H-nmr, ms, mp, mmp) with an authentic reference sample (Aldrich Chemical Company, Milwaukee, WI).

ISOLATION OF (2R-3-(PARA-HYDROXYPHENYL) LACTIC ACID (**1**).—Elution of column B with C_6H_6-Me_2CO (4:1) (350 ml) afforded (2*R*)-3-(*p*-hydroxyphenyl) lactic acid (**1**) (10 mg) mp 164-165° (C_6H_6-Me_2CO); $[\alpha]^{26}D$ −13° (c 0.15, MeOH); uv, λ max (MeOH), 286 nm (sh) (log ε 2.94), 278(3.03) and 225(3.55); ir, ν max (KBr) 3480 cm^{-1}, 3240, 1740, 1615, 1600, 1510, 1450, 1370, 1355, 1235, 1190, 1110, 1080, 1020, 965, 925, 830, 780, 730 and 710; ms, M^+ *m/z* 182 (5%), 137(4), 119(8), 107(100), 91(12), and 77(41) identical by direct

comparison (mp, uv, ir, ^{1}H-nmr, ms) with (±)-3-(*p*-hydroxyphenyl) lactic acid prepared by reduction of *p*-hydroxyphenylpyruvic acid (Aldrich Chemical Co.) in MeOH with $NaBH_4$ in the usual fashion (26) and by comparison of literature values [mp 169-170°; $[\alpha]^{26}D$ −19.6° (c 1.3, H_2O) (27)] of authentic (−)-3-(*p*-hydroxyphenyl)lactic acid.

ACKNOWLEDGMENTS

The authors are grateful to Professor Otto R. Gottlieb, Universidade De Sao Paulo, Brasil, for spectra of 7-hydroxyflavanone and 5-deoxykaempferol; Dr. Kenneth R. Markham, Department of Scientific and Industrial Research, Petone, New Zealand, for spectra of 4′,7-dihydroxyflavone; Professor D. Adinarayana, Sri Venkateswara University, Kurnool, India, for samples and spectra of numerous flavonoids, and Mr. Joseph Bender, School of Pharmacy, University of Pittsburgh, for determining the mass spectra. A.B. Ray and R. Maurya are grateful to the U.G.C., New Delhi, for financial assistance.

LITERATURE CITED

1. S.K. Jain, "Medicinal Plants," National Book Trust, New Delhi, India, 1968, pp. 116-118.
2. R.N. Chopra, I.C. Chopra, K.L. Handa, and L.D. Kapur, "Indigenous Drugs of India," 2nd edition. U.N. Dhur and Sons Private Limited, Calcutta, India, 1958, p. 522.
3. S.S. Gupta, *Indian J. Med. Res.*, **51**, 716 (1963).
4. D.S. Shah, *Indian J. Med. Res.*, **55**, 166 (1967).
5. B.K. Chakravarthy, S. Gupta, S.S. Gambhir, and K.D. Gode, *Ind. J. Pharmacol.*, **12**, 123 (1980).
6. B.K. Chakravarthy, S. Gupta, S.S. Gambhir, and K.D. Gode, *Indian Drugs*, 184 (1981).
7. B.K. Chakravarthy, S. Gupta, S.S. Gambhir, and K.D. Gode, *Lancet*, October 3, 759 (1981).
8. B.K. Chakravarthy, S. Gupta, S.S. Gambhir, and K.D. Gode, *Life Sci.*, **29**, 2043 (1981).
9. H. Kolb, U. Kiessel. B. Greulich, and J. VanderBosch, *Lancet*, June 5, 1303 (1982).
10. B.K. Chakravarthy, S. Gupta, and K.D. Gode, *Lancet*, July 31, 273 (1982).
11. B.K. Chakravarthy, S. Gupta, and K.D. Gode, *Life Sci.*, **31**, 2693 (1982).
12. E.W. Sheehan, M.A. Zemaitis, D.J. Slatkin, and P.L. Schiff, Jr., *J. Nat. Prod.*, **46**, 232 (1983).
13. E. Sheehan, D. Stiff, F. Duah, D. Slatkin, P. Schiff, and M. Zemaitis, *Life Sci.*, **33**, 593 (1983).
14. T.R. Seshardi, *Phytochemistry*, **11**, 881 (1972).
15. J. Mathew, A.V. Subba Rao, and N.V. Subba Rao, *Curr. Sci.*, **46**, 337 (1977).
16. D. Adinarayana and K.V. Syamasundar, *Phytochemistry*, **21**, 1083 (1982).
17. D. Adinarayana, K.V. Syamasundar, O. Seligmann, and H. Wagner, *Z. Naturforsch.*, **37C**, 145 (1982).
18. A.V. Subba Rao and J. Mathew, *Phytochemistry*, **21**, 1837 (1982).
19. P.N. Bhargava, *Proc. Ind. Acad. Sci.*, **24**, 496 (1946).
20. J.B. Harborne, T.J. Mabry, and H. Mabry, "The Flavonoids," Academic Press, New York, 1975, p. 563.
21. *Ibid.*, p. 269.
22. R. Maurya, A.B. Ray, F.K. Duah, D.J. Slatkin, and P.L. Schiff, Jr., *Heterocycles*, **19**, 2103 (1982).
23. K. Nakamura, M. Tadenuma, K. Motegi, T. Yoshie, and S. Sato, *Nippon Jozo Kyokai Zasshi*, **64**, 1092 (1969); *Chem. Abstr.*, **75**, 108438 (1971).
24. A.B. de Oliveira, L.G. Fonseca e Silva, and O.R. Gottlieb, *Phytochemistry*, **11**, 3515 (1972).
25. T.J. Mabry, K.R. Markham, and M.B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, New York, 1970, passim.
26. L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, 1967, pp. 1049-1051.
27. R.M.C. Dawson, D.C. Elliott, W.H. Elliott, and K.M. Jones, "Data for Biochemical Research," 2nd edition. Clarendon Press, Oxford, 1969, pp. 84-85.

Received 25 April 1983