

21)^b; 19.3(C-26)^b; 19.5(C-19); 20.1(C-27); 21.4(C-11); 23.5(C-28); 24.6(C-15); 26.5(C-23); 28.6(C-16); 29.6(C-25); 30.4(C-2); 32.2(C-7 and C-8); 34.3(C-22); 36.5(C-20); 37.0(C-10); 37.6(C-1); 39.4(C-12); 40.0(C-4); 42.6(C-13); 46.1(C-24); 50.4(C-9); 56.3(C-17); 56.9(C-14); 62.9(C-6^G); 71.7(C-4^G); 75.3(C-2^G); 78.1(C-3); 78.5(C-3^G); 78.6(C-5^G); 102.6(C-1^G); 121.9(C-6); 140.8(C-5) (^{a,b} these assignments may be interchanged).

Fraction 2 provided kaempferol 3-*O*- β -rutinoside that was repeatedly purified by column chromatography on silica gel H (ethyl acetate-ethanol) and Sephadex LH-20 (methanol). It was identified by hydrolytic and spectral data (8).

Fraction 3 yielded kaempferol 3-*O*- β -rutinoside 7-*O*- α -rhamnopyranoside (8,9,10), that was purified and characterized as mentioned above.

Treatment of both flavonoids with dichloromethyl methyl ether (11) confirmed the presence of rutinose.

These two flavonoids were also obtained from the ethanolic extract of fresh white flowers of *B. candicans*. The main component of this extract was 3-*O*-methyl-*D*-inositol (*D*-pinitol). Its spectra and physical data were concordant with those reported (12).

ACKNOWLEDGMENTS

We want to thank Prof. Emilio Ulibarri (Instituto de Botánica Darwinion, Argentina) for the identification of the plant material and Lic. Gustavo Aldomá for ¹H-nmr spectra.

We are also indebted to CONICET (Argentina) and CEFAPRIN (Argentina) for financial support.

LITERATURE CITED

1. J. Shani, A. Goldschmied, B. Joseph, Z. Ahronson, and F.G. Sulman, *Arch. Int. Pharmacodyn. Ther.*, **210**, 27 (1974).
2. G. Weiczal, P. Wahl, and E. Buddecke, *Z. Physiol. Chem.*, **327**, 109 (1962).
3. D. J. Luzbetak, S.J. Torrance, J.J. Hoffmann, and J.R. Cole, *Lloydia*, **42**, 315 (1979).
4. The Sadtler Standard Spectra, Sadtler Res. Lab. ¹H-nmr spectra No. 8809 (1968).
5. E. Larsen, H. Egsgaard, and H. Holmen, *Org. Mass Spectrom.*, **13**, 417 (1978).
6. A.N. Misra and H.P. Tiwari, *Phytochemistry*, **12**, 393 (1973).
7. A.K. Dzizenko, V.V. Isakov, N.I. Uvarova, G.I. Oshitok, and G.B. Elyakov, *Carbohydr. Res.*, **27**, 249 (1973).
8. K.R. Markham, B. Ternai, R. Stanley, H. Geiger, and T.M. Mabry, *Phytochemistry*, **34**, 1389 (1978).
9. H. Schels, H.D. Zinsmeister, and K. Pflieger, *Phytochemistry*, **16**, 1019 (1977).
10. H.-F. Aly and H. Geiger, *Phytochemistry*, **14**, 1613 (1975).
11. H. Gross and I. Farkas, *Chem. Ber.*, **93**, 95 (1960).
12. D.E. Dorman, S.J. Angyal, and J.D. Roberts, *J. Am. Chem. Soc.*, **92**, 1351 (1970).

Received 3 November 1982

THE ALKALOIDS OF *HUNNEMANIA FUMARIAEFOLIA*

M.A. EL-SHANAWANY,

*Department of Pharmacognosy, Faculty of Pharmacy,
University of Assiut, Assiut, Egypt*

A.M. EL-FISHAWAY, D.J. SLATKIN, and P.L. SCHIFF, JR.

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

Hunnemania fumariaefolia Sweet (Papaveraceae), also known as the tulip poppy or Golden Cup, is an ornamental herb usually cultivated as a garden plant for its bright yellow flowers (1). Extracts of the tops of this species have been found to inhibit the growth of a variety of microorganisms (2), with this antimicrobial activity subsequently assigned, via bioassay-guided isolation, to the alkaloidal artifacts sanguinarine pseudomethanolate and pseudoethanolate, chelerythrine pseudomethanolate and pseudoethanolate (3). Earlier investigations resulted in the isolation of numerous

alkaloids, including allocryptopine, berberine, chelerythrine, chelilutine, chelirubine, corysamine, escholidine, hunnemanine, and protopine (4-6) and the flavonol glycoside isorhamnetin-3 β -D-glucopyranosido-7 α -L-arabinopyranoside (7) from extracts of this plant.

Extraction, fractionation, and chromatography of this species has now resulted in the reisolation of the protopine alkaloids hummemanine, protopine, and allocryptopine and in the isolation of the isoquinolone alkaloid oxyhydrastinine (1-oxo-2-methyl-3,4-dihydro-6,7-methylenedioxyisoquinoline). Oxyhydrastinine has only recently been isolated from two papaveraceous species, *Argemone mexicana* L. (8) and *Papaver dubium* L. var. *glabrum* (8), and to our knowledge, this represents the first reported isolation of this alkaloid from a *Hunnemanina* species.

EXPERIMENTAL¹

PLANT MATERIAL.—The entire plant of *Hunnemanina fumariaefolia* Sweet (Papaveraceae) was gathered from the Medicinal Plant Experimental Station in Assiut, Egypt, in Spring 1979. A voucher specimen is on deposit at the Department of Pharmacognosy, Faculty of Pharmacy, University of Assiut, Assiut, Egypt.

EXTRACTION AND FRACTIONATION OF ALKALOIDS.—Air-dried, powdered plant (10 kg) was extracted to exhaustion with ethanol, and the dried ethanol extract was partitioned in the usual fashion (9) to afford a crude basic fraction (150 g). Chromatography of this fraction over silica gel (1 kg) and elution with petroleum ether-benzene (95:5) (1 liter) afforded allocryptopine (400 mg), mp 155° (uv, ir, ¹H-nmr, ms) while elution with petroleum ether-benzene (85:15) (1 liter) yielded protopine (2 g), mp 198-200° (uv, ir, ¹H-nmr, ms). Elution with petroleum ether-benzene (1:9) (1 liter) afforded oxyhydrastinine (800 mg), mp 85-86° (CHCl₃-MeOH); ¹³C-nmr 28.1 (t, C-4), 35.1 (q, NCH₃), 48.3 (t, C-3), 101.4 (t, CH₂O₂), 106.8 (d, C-5 or C-8), 108.2 (d, C-8 or C-5), 123.6 (s, C-8a), 133.4 (s, C-4a), 146.9 (s, C-7), 150.3 (s, C-6) and 164.5 (s, C-1); ms, M⁺ m/z 205 (45%), 162 (88), 134 (100), 104 (19) and 76 (26) identical by direct comparison (uv, ir, ¹H-nmr, ms, mp, mmp) with an authentic reference sample (10) and literature data (8, 11). Finally, elution with benzene-methanol (99:5) afforded hunnemanine (3.8 g); mp 203-205° (uv, ir, ¹H-nmr, ms).

ACKNOWLEDGMENTS

The authors are grateful to Mr. Joseph Bender, School of Pharmacy, University of Pittsburgh, for determining the mass spectra; to Professor Maurice Shamma, Department of Chemistry, The Pennsylvania State University for a sample of protopine and to Professor Frank R. Stermitz, Department of Chemistry, Colorado State University for samples of allocryptopine and hunnemanine. This investigation was supported in part by a Peace Fellowship Grant from America-Mideast Education and Training Services, Inc. with the authors M.A. El-Shanawany and A.M. El-Fishawy serving as Peace Fellows.

LITERATURE CITED

1. L.H. Bailey, "Manual of Cultivated Plants," The Macmillan Company, NY, 1954, p. 423.
2. L.A. Mitscher, R. Leu, M.S. Bathala, W. Wu, J.L. Beal, and R. White, *Lloydia*, **35**, 157 (1972).
3. L.A. Mitscher, Y.H. Park, D. Clark, G.W. Clark, III, P.D. Hammesfahr, W. Wu, and J.L. Beal, *J. Nat. Prod.*, **41**, 145 (1978).
4. R.H.F. Manske, L. Marion, and A.E. Ledinghorn, *J. Am. Chem. Soc.*, **64**, 1659 (1942).
5. L. Slavikova and J. Slavik, *Collect. Czechoslov. Chem. Commun.*, **31**, 1355 (1966).
6. J. Slavik, L. Dolejs, and P. Sedmera, *Collect. Czechoslov. Chem. Commun.*, **35**, 2597 (1970).
7. H. Wagner, M.A. Iyengar, O. Seligmann, J.L. Beal, and L. Mitscher, *Lloydia*, **36**, 166 (1973).
8. B.D. Krane and M. Shamma, *J. Nat. Prod.*, **45**, 383 (1982).
9. R.W. Doskotch, P.L. Schiff, Jr., and J.L. Beal, *Lloydia*, **32**, 29 (1969).
10. P.L. Schiff, Jr., Unpublished results. Oxyhydrastinine was synthesized in an analogous manner to thalifoline [R.W. Doskotch, P.L. Schiff, Jr. and J.L. Beal, *Tetrahedron*, **25**, 469 (1969)].
11. M. Shamma and D.H. Hindenlang, "Carbon-13 NMR Shift Assignments of Amines and Alkaloids," Plenum Press, NY, 1979, p. 116.

Received 20 December 1982

¹Full details of the isolation and identification of the compounds are available on request to the authors.