TERPENOIDS FROM *VIGUIERA LATIBRACTEATA* AND *VIGUIERA GREGGII*

GUILLERMO DELGADO,* LAURA ALVAREZ, RACHEL MATA,[1]
ROGELIO PEREDA-MIRANDA,[2] ALFONSO ROMO DE VIVAR,

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México, D.F.

and JOSE LUIS VILLASEÑOR

Instituto de Biología, Universidad Nacional Autónoma de México, Departamento de Botánica, Apartado Postal 70-367, 04510 México, D.F.

As part of our continuing chemosystematic studies of Mexican *Viguiera* species (1-4), we have examined aerial parts of *V. latibracteata* (Hemsl.) Blake and *V. greggii* (Gray) Blake (Compositae).

V. latibracteata (subgenus Amphilepsis) afforded eight *ent*-kaurenoid diterpenes, niveusin C (5), clovandiol, stigmasterol, and β-sitosterol. On the other hand, two *ent*-kaurenoid acids and the sesquiterpene lactones zexbrevin and zexbrevin B were isolated from a population of *V. greggii* (subgenus Calanticaria) (6). The last two substances were previously isolated from what was referred to as *Zexmenia brevifolia* Gray (7,8), but careful morphological reexamination of the original plant material used for chemical analysis (deposited in the National Herbarium) resulted in its identification as *V. greggii*. Therefore, the actual natural source of the zexbrevins (7-10) is *V. greggii*, not *Z. brevifolia*. The structures of the terpenoids here described are similar to those of other *Viguiera* species. While *ent*-kaurenoids are widely distributed in this and related genera, the presence of furane heliangolides is characteristic of some sections of the genus (11).

EXPERIMENTAL

PLANT MATERIAL.—*V. latibracteata* was collected in El Espinazo del Diablo, State of Durango, September 18, 1983 (voucher GD 1157), and *V. greggii* was collected near Saltillo, State of Coahuila, July 25, 1983 (voucher GD 1159). The herbarium specimen of *V. greggii* (previously misidentified as *Z. brevifolia*) has the voucher GD 1160. All the samples are maintained in the National Herbarium, Instituto de Biología de la Universidad Nacional Autónoma de México.

EXTRACTION AND ISOLATION.—Pulverized, dried aerial parts of *V. latibrateata* (3.2 kg) were extracted at room temperature with $CHCl_3$-Me_2CO (7:3), to give 108 g residue. Column chromatography of this extract over silica gel using hexane and mixtures of hexane/EtOAc, and subsequent rechromatographies, yielded *ent*-kaur-16-en-19-oic acid, zoapatlin, 15α-angeloyloxy-*ent*-kaur-16-en-19-oic-acid, 15α-*tigloyloxy-ent*-kaur-16-en-19-oic acid, stigmasterol, β-sitosterol, 15α,16α-epoxy-17-hydroxy-*ent*-kauran-19-oic acid, 15α-hydroxy-*ent*-kaur-16-en-19-oic acid, 17-hydroxy-*ent*-kaur-15-en-19-oic acid, niveusin C, clovandiol, and 16α,17-dihydroxy-*ent*-kauran-19-oic acid. Some acids were characterized as methyl esters.

Dried aerial parts of *V. greggii* (690 g) were extracted with $CHCl_3$ to give 25.1 g of residue. Chromatographic resolutions of this extract, using hexane/EtOAc gradient elution system yielded *ent*-kaur-16-en-19-oic acid, 15α-angloyloxy-*ent*-kaur-16-en-19-oic acid, zexbrevin, and zexbrevin B (yields range: $0.75\text{-}1\times10^{-3}$%). Full details of the isolation and identification data are available on request.

ACKNOWLEDGMENTS

We thank Consejo Nacional de Ciencia y Tecnología (CONACyT), México, for partial financial support.

LITERATURE CITED

1. L. Alvarez, R. Mata, G. Delgado, and A. Romo de Vivar, *Phytochemistry*, **24**, 2973 (1985).
2. G. Delgado, L. Alvarez, and A. Romo de Vivar, *Phytochemistry*, **24**, 2736 (1985).
3. G. Delgado, L. Alvarez, and A. Romo de Vivar, *Phytochemistry*, **23**, (1984).

[1]Present address: Departamento de Química Farmacéutica y Productos Naturales, División de Estudios de Posgrado de la Facultad de Química, Universidad Nacional Autónoma de México, Circuito Escolar, Ciudad Universitaria, Coyoacán 04510, México, D.F.

[2]Present address: Departamento de Química Orgánica de la Escuela Nacional de Ciencias Biológicas del Instituto Politécnico Nacional, México 11340, D.F.

4. G. Delgado, H. Cárdenas, G. Peláez, A. Romo de Vivar, and R. Pereda-Miranda, *J. Nat. Prod.*, **47**, 1042 (1984).
5. N. Ohno and T.J. Mabry, *Phytochemistry*, **19**, 609 (1980).
6. Y.L. Liu, J. Gershenzon, and T.J. Mabry, *Phytochemistry*, **23**, 1967 (1984).
7. A. Romo de Vivar, C. Guerrero, E. Díaz, and A. Ortega, *Tetrahedron*, **26**, 1657 (1970).
8. A. Ortega, C. Guerrero, A. Romo de Vivar, J. Romo, and A. Palafox, *Rev. Latinoam. Quím.*, **2**, 38 (1971).
9. A. Ortega, C. Vargas, C Guerrero, and A. Romo de Vivar, *Rev. Latinoam. Quím.*, **4**, 1 (1973).
10. A. Ortega, C. Guerrero, and J. Romo, *Rev. Latinoam. Quím.*, **4**, 91 (1974).
11. A. Romo de Vivar and G. Delgado, *Bol. Soc. Chil. Quím.*, **30**, 79 (1985).

Received 25 April 1986

ALKALOIDS OF *GLAUCIUM GRANDIFLORUM*

FATMA EL-AFIFI,* DAWUD AL-EISAWI,

Faculty of Pharmacy, University of Jordan, Amman, Jordan

SULEIMAN AL-KHALIL,[1] and PAUL L. SCHIFF, JR.*

Department of Pharmaceutical Sciences, School of Pharmacy, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Glaucium grandiflorum Boiss. and Huet (Papaveraceae) is a perennial herb indigenous to various regions of the Mideast extending from the eastern Mediterranean to Iran (1-3). Although numerous alkaloids with varying pharmacological activities have been isolated from approximately ten or so species of the genus *Glaucium*, there have been no reports of the presence of alkaloids or of their chemotaxonomic profile in the plant *G. grandiflorum* (4,5). An investigation of the alkaloid-containing fractions of an extract of the whole plant of *G. grandiflorum*, via column chromatography, led to the isolation of (−)-norchelidonine, dihydrochelerythrine, (−)-8-acetonyldihydrochelerythrine, protopine, allocryptopine, (±)-tetrahydrojatrorrhizine (corypalmine), and (±)-tetrahydropalmatine.

EXPERIMENTAL

PLANT MATERIAL.—The plant material used in this study was collected and identified by Dr. Dawud Al-Eisawi in April 1984, from the Irbid District, Yarmuk University, new permanent campus. Voucher specimens are on deposit at the Department of Pharmacognosy, Faculty of Pharmacy, University of Jordan, Amman, Jordan and at the Herbarium, Faculty of Science, Amman.

EXTRACTION AND ISOLATION.—Powdered, dried, whole plant (1.2 kg) was extracted by percolation with EtOH (10 liters). The extract was concentrated to a residue, stirred with aqueous citric acid and filtered, and the filtrate was extracted with Et_2O. The remaining aqueous solution was basified with NH_4OH and extracted with Et_2O, and the nonphenolic alkaloids (Fraction A) were separated from the phenolic alkaloids (Fraction B) in the usual manner (6). Chromatography of Fraction A over Si gel afforded (−)-norchelidonine (11 mg) (7,8), dihydrochelerythrine (3 mg)(7), (−)-8-acetonyldihydrochelerythrine (5 mg)(7,9), protopine (16 mg)(10), and allocryptopine (18 mg)(10). Chromatography of Fraction B over Si gel yielded (±)-tetrahydrojatrorrhizine (corypalmine) (4 mg)(11) and (±)-tetrahydropalmatine (5 mg)(11). The alkaloids were identified by direct comparison with authentic samples or comparison with literature data using accepted techniques (uv, ir, eims, mp, $[\alpha]_D$)(7-11).

Full details of the isolation and identification of the alkaloids are available from the senior authors upon request.

ACKNOWLEDGMENTS

The authors are grateful to Mr. James Dru, School of Pharmacy, University of Pittsburgh, and Dr. Alvin Marcus, Department of Chemistry, University of Pittsburgh, for determining the mass spectra; to Professor Luis Castedo, Facultad de Quimica, Universidad de Santiago, Spain, for spectra and a sample of (−)-norchelidonine; to Professor D.B. MacLean, Department of Chemistry, McMaster University, Hamilton, Ontario, Canada, for a sample of 8-acetonyldihydrochelerythrine; and to Professor Jose Lopez, Facultad de Farmacia, Universidad de Costa Rica, for a sample of chelerythrine.

[1]Current Address: Faculty of Pharmacy, University of Jordan, Amman, Jordan.