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PAPAVERACEAE

ALKALOIDS OF *ARGEMONE GLAUCA* VAR. *GLAUCA**

F. R. STERMITZ,† S. M. WORKMAN† and W. M. KLEIN‡

Departments of Chemistry and Botany and Plant Pathology, Colorado State University,
Fort Collins, Colorado 80521, U.S.A.

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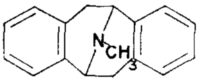
Abstract—*Argemone glauca* L. ex Pope, var. *glauca* from the island of Lanai, Hawaii was found to contain protopine, allocryptopine, sanguinarine, berberine, and chelerythrine as the major aklaloids. This alkaloid content corresponds with that expected from a more specialized *Argemone* species.

WE HAVE suggested[1] that, in species of the poppy genus *Argemone*, the major presence of alkaloids having the pavine-type skeleton (I) may indicate such species to be more primitive than those lacking such alkaloids. We have pointed to some of the Texas species and others such as *Argemone mexicana* (which has been spread throughout the harbor areas of the world) as more advanced. Most of these latter species contain allocryptopine (IIa), protopine (IIb), and berberine (III) as the major alkaloids, with little alkaloid variation among the species.[1]



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An interesting species for investigation was thought to be *A. glauca* L. ex Pope, var. *glauca*, which is restricted to Hawaii. Ownbey has pointed out[2] that this taxon was known to exist in Hawaii at the time of the discovery of the islands by Cook in 1778. The species shows considerable variation and Ownbey has described[2] two other varieties, one restricted to the island of Hawaii and the other to Kahoolawe. Carter has discussed[3] the anomalous presence of some purely American plants in Hawaii, the great majority of whose ancient flora is of Southeast Asian origin. Carter suggested[3] that the Hawaiian presence of *A. glauca*, which shows considerable morphological divergence from the mainland American *Argemone*, provided additional evidence for his contention that human occupancy of the

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† Department of Chemistry.

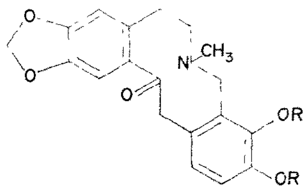
‡ Department of Botany and Plant Pathology.

[1] F. R. STERMITZ, D. E. NICODEM, C. C. WEI and K. D. MCMURTREY, *Phytochem.* **8**, 615 (1969).

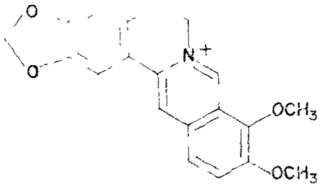
[2] G. B. OWNBEY, *Brittonia* **13**, 91 (1961).

[3] G. F. CARTER, in *Plants and Migration of Pacific Peoples* (edited by J. BARRAU), Bishop Museum Press, Honolulu, Hawaii (1963).

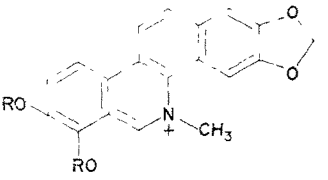
islands must have come from the Americas much earlier (2500 B.C.–1 A.D.) than was originally thought (500–1000 A.D.). The latter date of introduction would not have given *A. glauca* sufficient time to develop its present divergent characteristics.



IIa, R=CH_3 Allocryptopine
b, R=—CH_2— Protopine



III Berberine



IVa, R=—CH_2— Sanguinarine
b, R=CH_3 Chelerythrine

We suggested[1] that sufficient *Argemone* species have been chemically analyzed and these data compared with morphology so that predictions could be made about the alkaloidal content to be expected in uninvestigated species. Thus, we would have predicted *A. glauca* to contain allocryptopine, protopine, and berberine as the major alkaloids.

RESULTS

Analysis showed *A. glauca* var. *glauca* to contain 0·47% total alkaloids composed of the following: protopine (IIb), 40%; allocryptopine (IIa), 20%; sanguinarine (IVa), 20%; berberine (III), 10%; and chelerythrine (IVb), 10%.

DISCUSSION

The alkaloid content of *A. glauca* var. *glauca* was close to that predicted for a species of relatively late (among the *Argemone*) evolutionary development. Sanguinarine was present in a larger amount than previously found in some of the *Argemone*, but our techniques for isolation and estimation of this particularly difficultly isolable alkaloid have improved. Thus, the first test of the predictive value of our view[1] of *Argemone* systematics has been successful.* We would assign *A. glauca* to Alliance IVa.[3]

EXPERIMENTAL

Plants of *Argemone glauca* L. ex Pope, var. *glauca* were collected on the island of Lanai, Hawaii in July 1969. A voucher sample was deposited in the Colorado State University herbarium under accession No. 49190. A total of 1800 g of dried, ground plant material was wet with aq. $NaCO_3$ and then was extracted with 10 l. of benzene-$CHCl_3$ (1:1). The organic layer was separated and extracted with 5 l. of 1 M H_2SO_4. The acidic solution was brought to pH 8·6 and extracted five times with an equal vol. of $CHCl_3$. The $CHCl_3$ solution was dried with Na_2SO_4, filtered, and evaporated to dryness to yield 8·5 g (0·47% of the dried plant weight) of crude alkaloid mixture. The residue was recrystallized several times from methanol to yield protopine. After most of the protopine was removed, a 200 mg portion of residue was chromatographed on a

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* We predicted[3] that of the *Argemone* species remaining to be investigated only *A. fruticosa*, *A. subintegrifolia*, *A. echinata*, and *A. brevicornuta* might contain major amounts of pavine-type (I) alkaloids. We were recently able to observe and collect *A. fruticosa* and *A. echinata* in the field. *A. echinata* was earlier incorporated into either *A. platyceras* or *A. hispida*, but Ownby suggested (cf. Ref. 6) a possible alliance with *A. squarrosa*. Field observation of the plant makes this latter suggestion reasonable to us also. If the earlier view has validity, pavine-type alkaloids are expected, but they would not be expected if Ownbey's view is correct. *A. fruticosa* (which Ownbey was unable to examine in the field, cf. Ref. 6) appears to be more specialized than previously thought. If this is true, *A. fruticosa* will probably *not* be a good source of pavine-type alkaloids. Chemical analysis and chromosome studies on these species will be initiated soon.

[4] G. B. OWNBEY, Monograph of the Genus Argemone for North America and the West Indies, *Memoirs of the Torrey Botanical Club*, Vol. 21, The Seeman Printery, Durham, North Carolina (1958).

2000 μ 20 × 20 cm silica gel plate. A band at R_f zero (3:2, benzene–methanol) was extracted and yielded berberine. A band at R_f 0·35 yielded allocryptopine and a wide orange band at R_f 0·90 yielded sanguinarine. At the bottom of the orange band was a yellow band which yielded chelerythrine. All the alkaloids were identified by comparing the i.r., NMR, and mass spectra with those of authentic samples.* The amount of protopine present was estimated from the amount isolated and the relative amounts of the remaining alkaloids were estimated visually from analytical TLC (iodoplatinic acid visualization) of the residues.

* We are indebted to R. H. F. Manske for the authentic sample of chelerythrine.

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POLEMONIACEAE

NEW *C*-GLYCOSYLFLAVONES FROM *PHLOX DRUMMONDII*

T. J. MABRY, H. YOSHIOKA, SHARON SUTHERLAND and SUSAN WOODLAND

The Cell Research Institute and Department of Botany, University of Texas at Austin, Austin, Texas 78712 U.S.A.

and

W. RAHMAN, MOHD. ILYAS, J. N. USMANI and NAJAMA HAMEED

Department of Chemistry, Aligarh Muslim University, Aligarh, India

and

JEAN CHOPIN and M. L. BOUILLANT

Laboratoire de Chimie Biologique, Faculte des Sciences de L'Universite de Lyon, France

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Abstract—*O*-Rhamnosyl-6-*C*-Xylosyl derivatives of apigenin and luteolin were found to be the two major flavonoids of the flowers of *Phlox drummondii.*

WE REPORT the isolation and structure determination of *O*-rhamnosyl-6-*C*-xylosylapigenin and *O*-rhamnosyl-6-*C*-xylosylluteolin, major flavonoids in the flowers of *Phlox drummondii* Hook. When the water-soluble portion of the residue obtained from the ethanol extract of flowers of *P. drummondii* was chromatographed over polyamide,[1] two major flavonoids, I, m.p. 198° and III, m.p. 210°, were obtained pure. Both substances yielded rhamnose upon acid hydrolysis.

*O-Rhamnosyl-*6*-C-xylosylapigenin* (*III*). Acid hydrolysis of compound III, the higher melting natural product, gave, in addition to rhamnose, a substance (IV), m.p. 228°, which

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[1] T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer-Verlag, New York (1970).