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ALKALOIDS OF THE THREE SUBSPECIES OF *ARGEMONE PLEIACANTHA* GREENE[1]

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Abstract—The alkaloid contents of one population of *Argemone pleiacantha* Greene subsp. *pinnatisecta* Ownb., three populations of *A. pleiacantha* subsp. *pleiacantha*, and five populations of *A. pleiacantha* subsp. *ambigua* Ownb. were determined. Large differences in the kinds and amounts of alkaloids were found in most of the populations. Subspecies *pinnatisecta* was suggested to be the phylogenetically oldest of the three subspecies.

OWNBEY has divided[2] *Argemone pleiacantha* Greene into three subspecies: *pleiacantha*, *ambigua*, and *pinnatisecta*. As part of our continuing interest in the alkaloids of *Argemone* and the chemotaxonomy[3] of the genus, we have investigated the alkaloid content of these three subspecies. Our initial investigations[3] pointed to an interesting intermediate phylogenetic placement of *A. pleiacantha* between those species containing pavine-type alkaloids and those lacking such compounds. In addition, preliminary work showed a far greater heterogeneity of alkaloid content with both subspecies and geographical location than we had noted in any of the other *Argemone* species. We therefore undertook an extensive investigation of *A. pleiacantha*, the results of which are reported here.

RESULTS

Table 1 lists the investigated subspecies according to location of collection and the alkaloids isolated in each case. A few specific comments before discussing the general chemotaxonomic conclusions are perhaps in order. The main apparent result is that the alkaloid content varies not only with subspecies, but also with geographical location. This point is discussed more fully below. Another interesting result is the complete lack of argemonine (IIId) in the species although its presumed precursor[4] bisnorargemonine is found in rather high concentrations several times. Perhaps the most closely related species to *Argemone pleiacantha* is *A. gracilenta* Greene, and we recently[1] found the latter plant to contain 95 per cent of the total alkaloid content as argemonine. This presence or lack of the enzyme (still unknown and uninvestigated) which converts *ortho*-substituted hydroxy-methoxy compounds to dimethoxy derivatives distinguishes a number of other species of the genus (e.g.

[1] Part XI in the series "Alkaloids of the Papaveraceae". For Part X, see F. R. STERMITZ and K. D. MCMURTREY, *J. Org. Chem.* **34**, in press (1969). The present work was supported by grant GM15424 from the U.S. Public Health Service.

[2] 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).

[3] F. R. STERMITZ, in *Recent Advances in Phytochemistry* (edited by T. J. MABRY), Vol. 1, Chap. 5, Appleton-Century-Crofts, New York (1968).

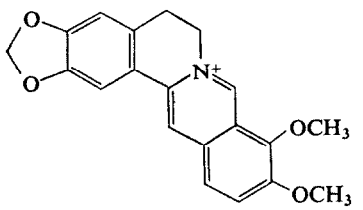
[4] F. R. STERMITZ and J. N. SEIBER, *J. Org. Chem.* **31**, 2925 (1966).

A. munita from *A. hispida*). Subspecies *pinnatisecta* represents an excellent source of munitagine (IIIb). This alkaloid has previously been reported[4] from only *A. munita* (about 40 per cent of the alkaloid content) and *A. gracilenta* (trace amounts). The bright yellow latex in the plants of all collections except subspecies *pinnatisecta* again[3] points to berberine as the main latex coloring constituent of the genus. The isolation of laudanosine (IV) from subspecies *pinnatisecta* is worthy of note since as far as we could ascertain the only reported other natural occurrence of this alkaloid is in *Papaver somniferum*, the opium poppy.

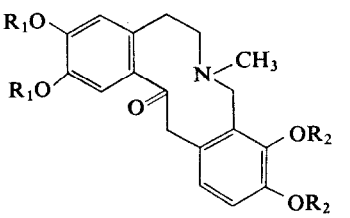
TABLE 1. ALKALOID CONTENT OF *Argemone pleiacantha* COLLECTIONS

Subspecies	Location	Percent of total alkaloids[a]						
		I	IIa	IIb	IIc	IIIa	IIIb	Other
ambigua	Peeples Valley, Arizona	30	—	25	—	20	10	—
ambigua	Prescott, Arizona	60	10	10	10	3	3	[b]
ambigua	Seneca, Arizona	45	20	—	30	3	1	[b]
ambigua	Ashfork, Arizona	30	25	25	—	*T*[c]	*T*[c]	—
ambigua	Miami, Arizona	*T*[c]	55	—	—	20	10	[b]
pleiacantha	Ashfork, Arizona	10	15	*T*[c]	—	45	10	[d]
pleiacantha	Sho Low, Arizona	50	35	—	15	—	—	[b]
pleiacantha	Hurley, New Mexico	60	15	—	10	—	—	[b]
pinnatisecta	High Rolls, New Mexico	—	—	—	—	15	75	

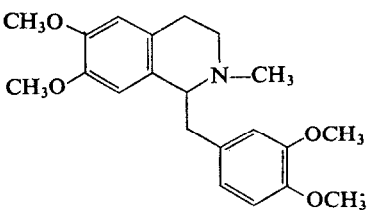
(a) Yields given are by actual isolation and were usually rounded to the nearest 5 per cent. (b) Traces of a mixture of highly polar, probably phenolic quaternary alkaloids were present. (c) *T*=trace. (d) A trace of norargemonine (IIIc) was also found. (e) About 5% of laudanosine (IV) and a trace of muramine (IId) were present.



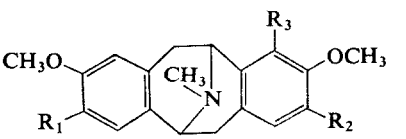
(I) Berberine



(IIa) Protopine ($R_1 = R_2 = —CH_2—$)
(IIb) Cryptopine ($R_1 = CH_3$; $R_2 = —CH_2—$)
(IIc) Allocryptopine ($R_1 = —CH_2—$; $R_2 = CH_3$)
(IId) Muramine ($R_1 = R_2 = CH_3$)



(IV) Laudanosine



(IIIa) Bisnorargemonine ($R_1 = R_2 = OH$; $R_3 = H$)
(IIIb) Munitagine ($R_1 = R_3 = OH$; $R_2 = H$)
(IIIc) Norargemonine ($R_1 = OCH_3$; $R_2 = OH$; $R_3 = H$)
(IIId) Argemonine ($R_1 = R_2 = OCH_3$; $R_3 = H$)

DISCUSSION

In our discussion[3,5] of the systematics of the genus, the presence or absence of berberine, protopine-type, and pavine-type alkaloids were proposed as criteria for alliances among *Argemone* species. This was an expansion of the original suggestion[6] of Slavik. It is apparent from Table 1 that *A. pleiacantha* could be placed in each of the three main alliances. Thus, subspecies *pinnatisecta* contains essentially only pavine-type alkaloids and is chemically related to *A. munita, hispida,* and *gracilenta.* Subspecies *ambigua* at the Peeples Valley and Miami, Arizona locations would belong to the intermediate alliance with *A. platyceras,* while the same subspecies from the other three Arizona collections would be related to *A. mexicana* and various members of the Texas *Argemone.* Subspecies *pleiacantha* shows the same diversity of alkaloid content with location. The alkaloid content of *A. pleiacantha* as a whole cannot be directly related to location since we were able to obtain both subspecies *ambigua* and subspecies *pleiacantha* from contiguous areas (east and south of Ashfork, respectively) and these were found to be considerably different chemically. We were also able to obtain subspecies *ambigua* from the Ashfork location both in 1965 and 1966 and found these collections to be essentially identical in alkaloid content. Morphologically, the various subspecies and even populations are sometimes very similar and sometimes show considerable variety. Thus, Ownbey commented[2] that the populations of subspecies *ambigua* in the Ashfork and Prescott areas might almost be recognized as separate subspecies and that there was a need for further study of these populations. Unfortunately, our chemical studies showed these two populations to be fairly similar in alkaloid content and hence our results can be considered as either not having contributed to solving this problem or as suggesting that these populations should not be separated.

The subspecies *pinnatisecta* represents an interesting case. It is known from only one occurrence and therefore could not be obtained from separated geographical locations. It is isolated from the other subspecies which, although not overlapping in geographical extent, are at least close to being contiguous to each other. The occurrence of *pinnatisecta* in the mountains of south central New Mexico represents a rather severe separation from the other subspecies of *A. pleiacantha.* Its alkaloid content suggests to us that this subspecies is phylogenetically earlier than the other subspecies and represents a bridge to the older alliance: that of *A. munita, A. hispida,* and *A. gracilenta.* Separation and diversification then could have led to the other subspecies, some of which have chemically evolved to the point that they form a bridge to the most recent alliance: that of *A. mexicana* and the Texas *Argemone.* These general points can be viewed in the overall context in the accompanying paper.[5]

It is important to point out that *A. pleiacantha* is the only species in which we have found such extensive diversification of alkaloid content, although a more complete study of *A. sanguinea* Greene[5] would possibly yield a similar result.

EXPERIMENTAL

General chemical experimental procedures, instrumentation, and proof of alkaloid structures were as described previously.[1,4] All alkaloids isolated were spectrally compared with authentic known compounds.

In order to avoid differences in plants due to stage of growth and to assist in identification, plants were collected which exhibited buds, flowers, and capsules. This method was successful in all cases except that of *Argemone pleiacantha* subsp. *pleiacantha* from Show Low, Arizona. We were unable to procure these at the above stage of growth and our collection consisted only of young plants which occasionally exhibited buds

[5] F. R. Stermitz, D. E. Nicodem, C. C. Wei and K. D. McMurtrey, *Phytochem.* **8**, 615 (1969).
[6] J. Slavik and L. Slavikova, *Coll. Czech. Chem. Commun.* **28**, 1728 (1963).

and flowers, but no capsules. Collections were made at exact locations personally visited and specified[2] by Ownbey and voucher samples were collected in each location. For alkaloid analysis, all above-ground parts were collected and combined. Analyses were generally performed on 1–4 kg of dried and ground plant material.

COLLECTIONS

Subspecies	*Location and Date*	*Herbarium No.*
ambigua	Yavapai Co., Ariz.; 1 mi. e. of Ashfork (6/13/65)	107939
	Yavapai Co., Ariz.; 1·8 mi. e. of Ashfork (6/07/66)	111083
ambigua	Yavapai Co., Ariz.; Peeples Valley at Paulden (6/13/65)	107542
ambigua	Yavapai Co., Ariz.; n. outskirts of Prescott (6/07/66)	111147, 111148
ambigua	Coconino Co., Ariz.; 3 mi. s.w. of Miami (6/14/65)	107555, 107556
pleiacantha	Yavapai Co., Ariz.; 1·8 mi. s. of Ashfork (6/07/66)	111151, 111152
pleiacantha	Navajo Co., Ariz.; 10 mi. s.w. of Show Low (6/09/66)	111085, 111086
pleiacantha	Grant Co., N.M.; 15 mi. s. of Hurley (6/17/66)	111153
pinnatisecta	Otero Co., N.M.; 1 mi. e. of tunnel on U.S. 82 at High Rolls (6/16/66)	111154