

ALKALOIDS FROM IRAQI SPECIES OF PAPAVERACEAE

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ABSTRACT.—Ten species of *Papaver* (*P. persicum*, *P. acrochaetum*, *P. armeniacum*, *P. curviscapum*, *P. glaucum*, *P. macrostomum*, *P. bornmuelleri*, *P. rhoeas*, *P. dubium*, *P. hybridum*), two species of *Glaucium* (*G. corniculatum*, *G. grandiflorum*) and *Roemeria hybrida*, which are native to Iraq, have been examined for their alkaloid contents. *P. acrochaetum*, *P. bornmuelleri* and *P. curviscapum* are not listed previously in the chemical literature for alkaloidal constituents. The following 21 alkaloids were obtained from small samples which were mainly of herbarium material:—mecambrine (1), roehybrine (2), floripavidine (3), *N*-methylasimilobine (4), roemerine (5), corydine (6), isocorydine (7), roemerine *N*-oxide (8), dehydroroemerine (9), liriodenine (10), alpinigenine (11), rhoeagenine (12), rhoeadine (13), glaucamine (14), glaudine (15), protopine (16), cryptopine (17), allocryptopine (18), cheilanthifoline (19), berberine (20), narcotine (21).

Numerous alkaloids have been isolated from species of Papaveraceae and excellent reviews on this subject have been published (1, 2). The presence of different chemical strains or races has been demonstrated for several species, e.g., from the genus *Papaver*, species of the sections *Oxytona* (3) and of *Miltantha* (4, 5, 6). Volume 4 of the new *Flora of Iraq* is now due to be published and contains a review of Iraqi Papaveraceae (7). Some 15 species of *Papaver*, 5 species of *Glaucium*, 2 species of *Roemeria* and 3 species of *Hypecoum* are native to Iraq. Although many species of these genera have been investigated for alkaloids, no detailed investigations have been made on the plants which grow in Iraq. In view of the successful application of analytical techniques for the identification of alkaloids from small samples of plant material obtained from herbarium sheets (8) and also because of the known variation in alkaloid content of some papaveraceous species, it was decided to screen herbarium samples of as many Iraqi species as possible for the presence of alkaloids. Herbarium samples of *Papaver*, *Glaucium*, and *Roemeria*, representing replicate collections, have been made available for chemical studies by the National Herbarium of Iraq and the College of Agriculture Herbarium, University of Baghdad. Many of these actual specimens represent collections listed in the new *Flora of Iraq* (7). In addition to the herbarium material, a few small samples of *Papaver* species were also made available for these chemical studies.

RESULTS AND DISCUSSION

The identification of alkaloids extracted and the yields obtained from some 36 samples of Iraqi papaveraceous species are given in table 1. The samples represent 10 of the 15 species of *Papaver*, 2 of the 5 species of *Glaucium* and 1 of the 2 species of *Roemeria* which are native to Iraq (7). Thirty of the samples were obtained from herbarium specimens ranging in weight from 0.1 g to 6.29 g

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TABLE 1. Alkaloids of Iraqi Papaveraceae species—sample data, results of alkaloid yields and identifications.

Species* collector's number (date collected)	Locality	Weight in g (plant part ^b)	Extract weight in mg (%) Dragendorff reaction ^c		Alkaloids ^d
			Non-phenolic	Phenolic	
PAPAVER Section MILTANTHA <i>P. persicum</i> Lindl.*					
Rawi 23294 ^f (6.7.1957)	Khanfur, N.E. of Zakho, c. 1200 m. mountain slope	1.12 (c)	8.5 (0.76) ++++	1.3 (0.12) +++	NP (c, l, s)—alpinigenine (m), rhoeadine (tm), glaudine (tm), unident. alk.
		4.27 (l, s)	5.3 (0.12) ++++	1.3 (0.03) +	
Rawi 23631 ^f (8.7.1958)	Zawita, N.E. of Zakho, 1880-2060 m, mountain	6.08 (l, s, f)	6.5 (0.11) ++++	2.7 (0.04) ++++	Total alk. (l, s, f)—floripavidine (tm), <i>N</i> -methylasimilobine (m), alpinigenine (m), narcotine (tm).
<i>P. acrochaetum</i> Bornm. Emberger, Guest, Long, Schwan and Serkahia 15483 ^f (1.5.1956)	Rowanduz Gorge, nr. Balikian, 650 m northern ledges	6.29 (c, l, s)	5.5 (0.09) ++++	0.8 (0.01) +++	NP—rhoeagenine (tm), unident. aporphine (M ⁺ 339), unident. 1-benzyltetrahydroisoquinoline (<i>m/e</i> 206), protopine (t), unident. alk. P—unident. rhoeadine-type (M ⁺ 371), unident. alk.
<i>P. armeniacum</i> (L.) DC Id. 26765 ^f (20.8.1950)	Qandil range, mountain slope	0.49 (r)	3.0 (0.61) +++	1.1 (0.22) =	NP—3 unident. alks. P—1 unident. alk.
		0.11 (c)	6.2 (5.6) ++++	0.8 (0.72) ++	NP—floripavidine (t), rhoeagenine (t) P—unident. alk.
		5.36 (l, s)	19.5 (0.36) ++++	1.0 (0.02) ++++	NP—floripavidine (mn), cryptopine (m), rhoeagenine (m). P—4 unident. alks.
		1.84 (r)	5.0 (0.27) ++++	0.6 (0.03) ++	NP—floripavidine (t), rhoeagenine (t), 2 unident. alks. P—1 unident. alk.
Gillett 9617 ^f (5.8.1947)	Algurd Dagh, 2500 m, S.E. slope	0.32 (c)	1.6 (0.10) ++++	—	NP—floripavidine (t), identical with Id 26765 (t).
		1.54 (l, s)	5.6 (0.36) ++++	—	NP—floripavidine (t), 4 unident. alks.
<i>P. curviscapum</i> Nabk. Rawi 8741 ^f (15.5.1947)	Matina (Chiya-i Matin) 1200 m	0.35 (c)	1.2 (0.34) +++	—	NP—allocryptopine (t), protopine (t)
		1.94 (l, s)	6.4 (0.33) ++++	2.7 (0.14) ++	NP—allocryptopine (tm), protopine (tm), unident. aporphine (M ⁺ 337), 3 unident. alks.
					P—unident. 1-benzyltetrahydroisoquinoline (<i>m/e</i> 206).
Section PAPAVER <i>P. glaucum</i> Boiss. et Hausskn.					
Rawi 22146 ^f (15.6.1957)	10 km W of Tawila, 1400 m, hillside	0.9 (c)	—	—	
		2.74 (l, s)	1.0 (0.04) =	—	
		0.43 (r)	—	—	

TABLE 1. Continued.

Species* collector's number (date collected)	Locality	Weight in g (plant part*)	Extract weight in mg (%) Dragendorff reaction ^c		Alkaloids ^d
			Non-phenolic	phenolic	
Rawi 22146 ^f (15.6.1957)	Duplicate sample but slightly different capsules	0.45 (c)	4.5 (1.0) ++++	—	NP (c, l, s)—liriodenine (mnui), roemerine (m), dehydroroemerine (m), roemerine <i>N</i> -oxide (m), unident. alk.
		0.95 (l, s)	6.1 (0.64) ++++	0.8 (0.08) ±	
Gillett and Rawi 7046 ^f (28.3.1947)	S. bank of Euphrates, opposite Rawa, 150 m.	0.18 (c)	0.5 (0.27) +	—	NP (c, l, s, f)—mixture unident. rhoeadine-types (m).
		0.69 (l, s, f)	1.6 (0.23) ++++	—	
		0.13 (r)	—	—	
S. Jasim s.n. (— .4.1977)	1 km N. of Rawunduz	0.25 (c)	1.6 (0.64) ±	—	NP (l, s, f, r)—3 unident. aporphines (M ⁺ 339; M ⁺ 325; M ⁺ 323), 4 unident. alks.
		7.03 (l, s, f, r)	11.6 (0.16) ++++	0.5 (0.01) +++	
A. Nakash (8.4.1977)	10 km S. of Rutba	0.58 (c, l, s, r)	4.2 (0.72) +++	—	NP (c, l, s, r)—rhoeagenine and/or glaucamine (m), unident. alk. (M ⁺ 275). P—unident. alk.
E.D. and F.A. Barkley 5160 ^f (20.4.1963)	R. Silwan, 7 km S. of Darbandi-i Khan	0.24 (c)	0.9 (0.37) ±	—	
SECTION CARATINAE					
<i>P. macrostomum</i> Boiss. et Huet					
Id. 28206 ^f (7.5.1959)	Haibat Sultan Dagh, 850 m	0.10 (c)	—	—	
		1.10 (l, s, f, r)	—	—	
A. Askari s.n. (— .4.1972)	Darbani-Bazyan, 5 km N.W. of the pass	0.57 (c)	—	—	
		5.26 (l, s, f)	—	—	
A. Askari s.n. (1.5.1977)	Bakra-jo, Sulaymania, nr. Experimental Station, 800 m.	1.21 (c)	—	—	
		3.01 (r)	1.6 (0.05) ±	—	
		51.32 (l, s, f)	4.5 (0.01) ++++	2.7 (0.01) +	
A. Askari (s.n.) (— .5.1973)	Nr. Said-Sadiq, between Sulaymaniyah and Halbjja, 800 m	0.5 (c)	—	—	NP—6 unident. alks.
		20.72 (l, s, f, r)	2.0 (0.01) +	—	
<i>P. bornmuelleri</i> Fedde					
S. Jasmin s.n. (— .4.1977)	1 km N. of Rawunduz	0.14 (c)	—	—	
		1.21 (l, s, f, r)	—	—	
Section ORTHORHOEADES					
<i>P. rhoeas</i> L.					
S. Omar 34250	Amrah, 120 km	4.04	5.5 (0.14)	2.7 (0.07)	NP—protopine (m), 2 un-

TABLE 1. Continued.

Species* collector's number (date collected)	Locality	Weight in g (plant part ^b)	Extract weight in mg (%) Dragendorff reaction ^c		Alkaloids ^d
			Non-phenolic	Phenolic	
(10.4.1966)	N.W. of Rutba, 650 km, in wheat-field	(l, s, f)	+++	+	ident. aporphines (M ⁺ 337; M ⁺ 339). P—unident. 1-benzyltetrahydroisoquinoline (<i>m/e</i> 192), unident. alk. NP—liriodenine (t)
Gillett 10842 (22.5.1948)	Tell Kotchek, Mosul liwa, 400 m	0.79 (c, l, s, f)	1.4 (0.17) ++++	—	
F. A. Barkley 2196 (4.5.1962)	8 km W. of K3, Ramadi	0.40 (c, l, s)	0.6 (0.15) +	—	NP—3 unident. alks.
S. Jasim s.n. (2.5.1977)	Makmor, W. slope of mountain	1.55 (c)	1.4 (0.09) ++++	—	NP—3 unident. alks.
	Kara-Choeh, nr. Asfand village	34.62 (l, s)	39.0 (0.11) ++++	7.5 (0.02) ++++	NP—roemerine (m), mecambaine (tm), dehydroroemerine (m), 7 unident. alks. P—6 unident. alks. NP—2 unident. alks.
Barkley and Haddad 5493 ^f (7.5.1963)	Nr. Mosul, river bottom	0.35 (l, s, f)	1.0 (0.29) ++	—	
<i>P. dubium</i> L. Gillett 11,119 ^f (26.5.1948)	Balad Sinjar. N. of the town 900-1300 m	1.79 (c, l, s, r)	—	—	
Section ARGEMONORRHOEDES					
<i>P. hybridum</i> L. Gillett and Rawi 6909 (26.3.1947)	Haditha, Duleim liwa, 140 m, irrigated field	1.59 (l, s, f)	0.6 (0.04) =	—	NP—3 unident. alks.
		0.23 (r)	2.0 (0.86) +++	—	NP—glauanine (tm), glaucamine (tm), 2 unident. alks. NP—3 unident. alks.
Gillett and Rawi 10286 ^f (20.3.1948)	Tuz Khormatu, Kirkuk liwa, 250 m, barley field	4.40 (l, s, f)	8.4 (0.19) +	—	
		0.61 (r)	—	—	
Barkley and Haddad 7407 ^f	19 km S. of Durbandi-i Khan, Kirkuk liwa, hilltop	0.44 (c, l, s, r)	—	—	
GLAUCIUM					
<i>G. corniculatum</i> (L.) Rud. subsp. <i>corniculatum</i> Rawi 20941 ^f (7.6.1957)	260 km N.W. of Ramadi, 500 m, hillside	1.43 (c)	11.0 (0.77) ++++	—	NP—allocryptopine (t), protopine (t), unident. alk. NP—allocryptopine (t), protopine (t), 4 unident. alks.
		1.76 (l, s, f, r)	13.8 (0.78) ++++	—	
Rawi 21224 ^f s (9.6.1957)	2 km N.W. of Rutba, 750 km gravel soil	2.22 (c)	12.5 (0.56) ++++	0.7 (0.03) ++	NP—allocryptopine (t), protopine (t), unident. alk. P—2 unident. alks.
		4.33 (l, s, f, r)	7.5 (0.17) ++++	2.4 (0.06) +	NP—allocryptopine (tm), protopine (tm), berberine (tm) 3 unident. alks. P—3 unident. alks.
Id. 41940 (16.3.1975)	50 km N. of Ramadi, 155 m, sandy gravel	4.18 (l, s, f)	26.3 (0.63) ++++	3.7 (0.09) ++++	NP—allocryptopine (tm), protopine (tm), unident. alk. M ⁺ 351; <i>m/e</i> 338, 320), unident. alk. (M ⁺ 337), berberine (t). 2 unident. alks. P—unident. aporphine (M ⁺ 327, <i>m/e</i> 326, 312, 310, 296).

TABLE 1. *Continued.*

Species* collector's number (date collected)	Locality	Weight in g (plant part ^b)	Extract weight in mg (%) Dragendorff reaction ^c		Alkaloids ^d
			Non-phenolic	Phenolic	
		0.49 (r)	6.2 (1.26) ++++	1.1 (0.22) ++	NP—allicryptopine (t), protopine (t), 4 unident. alks. P—unident. alk.
Rawi 31327 (14.5.1961)	160-190 km N.W. of Ramadi, 550 m, roadside	0.84 (l, s, f, r)	10.7 (1.20) ++++	1.4 (0.17) =	NP—allicryptopine (t), protopine (t). 2 unident. alks.
<i>G. corniculatum</i> (L.) Rud. subsp. <i>refractum</i> (Nab.) Cullen ^b					
Rawi, Khatib and Tikriti 29286 ^f (23.6.1960)	2 km N. of Mainiya, between Najf and Shabicha	0.74 (c)	12.5 (1.60) ++++	2.4 (0.32) ++++	NP—allicryptopine (t), protopine (t), 2 unident. alks. P—3 unident. alks.
		5.43 (l, s)	24.0 (0.44) ++++	6.4 (0.12) ++++	NP—allicryptopine (tm), protopine (tm), corydine (mun), 3 unident. alks. P—unident. alk. (M ⁺ 327).
<i>G. grandiflorum</i> Boiss. et Huet					
Gillet 10851 ^f (22.5.1948)	Kursi, 700 m, oak wood	3.89 (l, s, f, r)	14.8 (0.38) ++++	—	NP—allicryptopine (tm), protopine (tm), unident. alk. M ⁺ 351, m/e 336, 320, 2 unident. alks.
Chakrovarty, Rawi, Khatib and Alizzi 33090 ^f (13.4.1964)	105 km S.W. of Sinjar	6.63 (l, s, f)	20.3 (0.31) ++++	1.0 (0.02) +	NP—allicryptopine (tm), protopine (tm), isocorydine (m), berberine (tm), 2 unident. alks. (M ⁺ 365; M ⁺ 381), 2 unident. alks.
Chakrovarty, Rawi, Khatib and Alizzi 31701 (30.3.1962)	12 km S.E. of H2, bottom of Hawran Valley, 320 m	0.79 (c) 3.48 (l, s, f)	5.0 (0.63) ++++ 16.5 (0.47) ++++	0.3 (0.04) + 3.4 (0.10) +	NP—allicryptopine (t), protopine (t) NP—allicryptopine (t), protopine (t), 2 unident. alks. P—2 unident. alks.
ROEMERIA					
<i>R. hybrida</i> (L.) DC. subsp. <i>hybrida</i>					
Chakravarty, Rawi, Khatib and Alizzi 32082 ^f	Baidha, 78 km S. of Sinjar, 260 m	0.64 (c) 2.73 (l, s, f, r)	2.0 (0.31) =	— 3.0 (0.10) +++	NP—roehybrine (m), 2 unident. alks.
F. R. Bharucha and H. A. Ani s.n.	Nr. Lake Tharthar	0.42 (c, l, s)	0.7 (0.16) +++	0.3 (0.07) =	NP—roehybrine (t), 2 unident. alks.

**Papaver* species are arranged in the same order as in the Flora of Iraq (7).

^bPlant part abbreviations, c=capsules, f=flowers, l=leaves, r=roots, s=stems.

^cFor details of extraction methods and alkaloid tests see Experimental; — indicates a -ve reaction to Dragendorff reagent, any small weight of extract obtained is not recorded.

^dAbbreviations used: NP=non-phenolic alkaloid extract, P=phenolic alkaloid extract, t=tlc, u=uv, m=ms, i=ir, n=¹H nmr, unident.=unidentified, alk.=alkaloid.

^eIn the Floras of Iraq (7) and Iran (22), *P. tauricolom* Boiss. is listed as a synonym of *P. persicum* Lindl. In the Flora of Turkey (23), *P. tauricola* is listed as a separate species although it is stated that it may possibly not be distinct from the Iranian species *P. persicum*.

^fSpecimen cited in the Flora of Iraq (7).

*Syn. *G. phoeniceum* Crantz (7).

^bSyn. *G. refractum* Nab. (7).

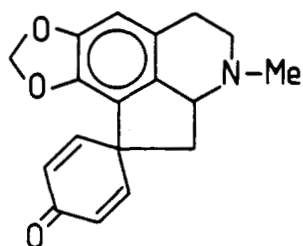
(table 1). Twenty of the 36 samples represent actual specimens listed in volume 4 of the new *Flora of Iraq* (7). The remaining 6 samples which were examined were not herbarium specimens, but, again, they were mainly available in low weights ranging from 0.14 g to 7.03 g. Larger quantities of between 20 g to 52 g were available for 2 samples of *P. macrostomum* and 1 sample of *P. rhoeas*. Wherever possible, each of the 36 samples was divided into capsules, leaves/stems/flowers, and roots. In table 1 the *Papaver* species are arranged in their sections following the same order in which they are listed in the new *Flora of Iraq* (7).

Alkaloid extracts were divided into non-phenolic and phenolic portions, and assessments of the amounts of alkaloid present were made on the basis of comparisons of color reactions with extracts and with known amounts of codeine to Dragendorff's reagent. These results are based on an arbitrary scale ranging from + to +++++ (see Experimental and table 1). The majority of the extracts gave results of +++++ but, surprisingly, some samples yielded extracts which were either very weak or even negative to Dragendorff's reagent, e.g., *P. glaucum*, *P. macrostomum*, *P. bornmuelleri*, *P. dubium*, and *P. hybridum* (see table 1). Those extracts which gave positive reactions to Dragendorff's reagent were examined by tlc; the number of alkaloidal spots are recorded in table 1. Tlc plates were sprayed with Dragendorff's reagent and also with 60% sulfuric acid which, on heating, gives colors which may be diagnostic for particular types of alkaloids (6). Some of the major alkaloids were separated from the extracts by preparative tlc and identified by mass spectrometry (ms). In some instances further confirmation of alkaloid identity was obtained from ^1H nmr, uv, and ir spectroscopy.

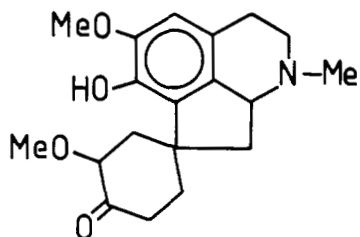
Reference to table 1 shows that some 21 alkaloids representing 6 different isoquinoline-types were identified. Two proaporphines, mecambrine (1) and roehybrine (2), and eight aporphines, floripavidine (3), *N*-methylassimilobine (4), roemerine (5), corydine (6), isocorydine (7), roemerine *N*-oxide (8), dehydro-roemerine (9) and liriodenine (10), were isolated. From the rhoeadine series, alpinigenine (11), rhoeagenine (12), rhoeadine (13), glaucamine (14), and glaudine (15) were obtained. Three protopine alkaloids, protopine (16), cryptopine (17), and allocryptopine (18), two berberine-types, cheilanthifoline (19) and berberine (20) and the phthalideisoquinoline alkaloid narcotine (21) were also identified. The majority of these alkaloids (1-21) were identified by direct comparison on tlc (R_f values and color reactions) and by their ms which were identical with reference alkaloids (see Experimental). Further confirmation of the identities of floripavidine (3), liriodenine (10) and corydine was obtained from their ^1H nmr spectra.

Floripavidine (3) and *N*-methylassimilobine (4) are rare *Papaver* alkaloids, although the latter (4) has been reported recently to be the major alkaloid of Egyptian *P. rhoeas* (9). Floripavidine was isolated originally from *P. floribundum* Desf. (10), which is a synonym of *P. fugax* Poir. (7). In the present work, floripavidine is shown to be present also in the related *Miltanthea* species, *P. persicum* Lindl. (syn *P. tauricum* Boiss.) and in *P. armeniacum* (L.) DC (table 1). Some of the δ values obtained from the ^1H nmr spectrum of floripavidine isolated in the present work differ from those reported previously (10, 12). Confirmation of identification of floripavidine (3) was obtained by hydrolysis to *N*-methyl-assimilobine (4). Roemerine (5) is a common alkaloid found in numerous *Papaver* species, but its *N*-oxide does not appear to have been isolated as a natural product. Roemerine *N*-oxide (8) is here reported as a constituent of *P. glaucum*. Liriodenine (10) is widely distributed in the plant kingdom and has been isolated from genera

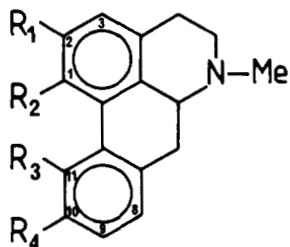
of Annonaceae, Araceae, Lauraceae, Magnoliaceae, Menispermaceae, Monimiaceae, Nymphaeaceae, Papaveraceae and Rutaceae (11, 12). Surprisingly, liriodenine (10) is not widely reported from species of Papaveraceae having been obtained from *Roemeria* (11) and from *P. heldreichii* (2). In the present investigation, liriodenine was identified from *P. glaucum* and *P. rhoeas* (table 1). Cheilanthe-



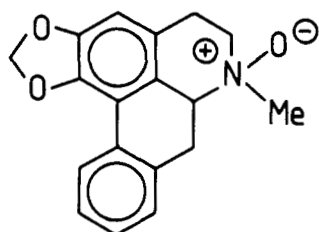
1 mecambrine



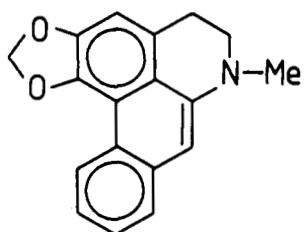
2 roehybrine



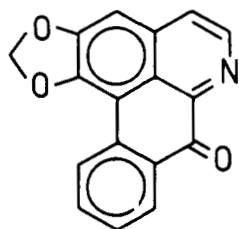
	R ₁	R ₂	R ₃	R ₄
<u>3</u> floripavidine	rhamnose	OMe	H	H
<u>4</u> <u>N</u> -methylasimilobine	H	OMe	H	H
<u>5</u> roemerine	-OCH ₂ O-		H	H
<u>6</u> corydine	OMe	OH	OMe	OMe
<u>7</u> isocorydine	OMe	OMe	OH	OMe



8 roemerine N-oxide



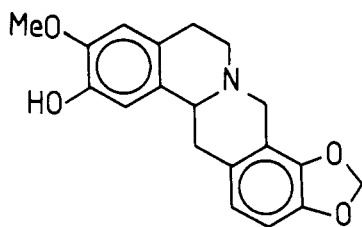
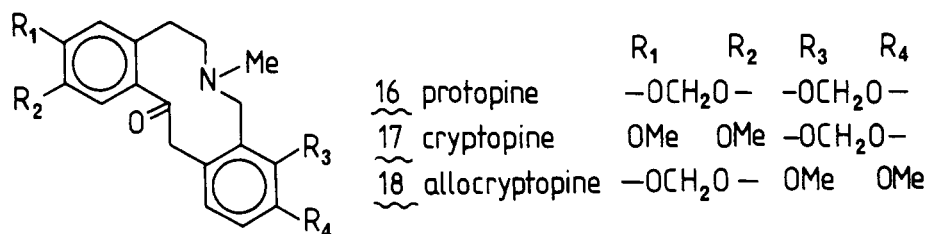
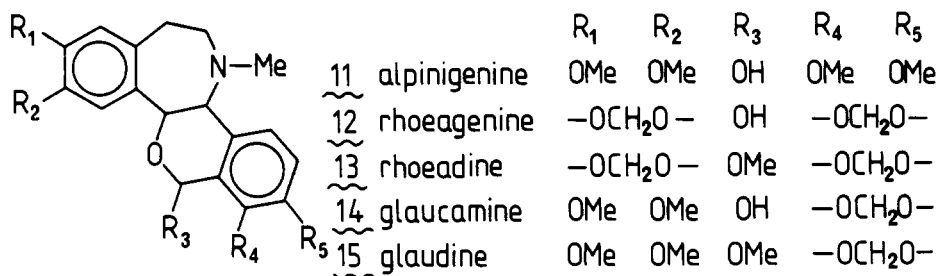
9 dehydroroemerine



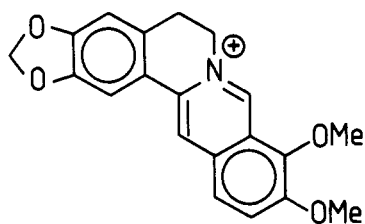
10 liriodenine

foline (19) is known to be present in species of *Argemone*, *Corydalis* and *Fumaria* but is not listed as a constituent of *Papaver* species in two major review articles (1, 2).

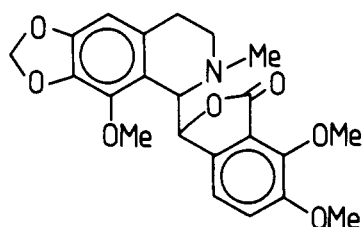
Despite the considerable volume of published data on *Papaver* alkaloids, there remain a number of species which are not listed in the chemical literature. Two species of the section *Miltanthea*, *P. acrochaetum* (rheagenine (12) and protopine



19 cheilanthifoline



20 berberine



21 narcotine

(16) identified—see table 1) and *P. curviscapum* (protopine (16) and allocryptopine (18) identified—see table 1) were not listed in the two major review articles on *Papaver* alkaloids (1, 2). Another species which does not appear in these two reviews is *P. bornmuelleri*; only 1.2 g was available in the present work, and the alkaloid results were negative (table 1). This result is probably an indication of a low alkaloid-yielding strain rather than the complete absence of alkaloids.

The major alkaloids of the two samples of *P. persicum* which was investigated proved to be of two different types (table 1). One sample contained rhoeadine-type alkaloids alpinigenine (11), rhoeadine (13) and glaudine (15); the other sample contained aporphines floripavidine (3) and *N*-methylassimilobine (4), although some alpinigenine was also present in the latter sample. These findings are similar to those reported for Turkish *P. tauricola* (syn. *P. persicum* in the Flora of Iraq) (7) which exists in at least two chemical strains (5). Floripavidine (3) was the major alkaloid of the two samples of *P. armeniacum* which were investigated, although rhoeagenine (12) and cryptopine (17) were also obtained.

A number of unidentified alkaloids were obtained from the four examined species of *Miltanthea*. In some instances ms data was sufficient to indicate the alkaloid type but did not allow for complete identification. The phenolic alkaloid obtained from *P. tauricum* (Rawi 23294) (table 1) with M^+ 327 had a large peak at m/e 326 in the ms and is probably an aporphine alkaloid with NMe and 2 x OMe substitution pattern (11, 12). The mass fragmentation of the alkaloid with M^+ 371 indicated a desmethylglucamine-type with MeO/OH substitution in ring A and OCH₂O substitution in ring C (5); the same alkaloid is present in *P. acrochaetum*. Another unidentified *P. acrochaetum* alkaloid gave an ms with M^+ at 339 and ion peaks corresponding to M^+-1 , M^+-15 and M^+-31 fragments indicative of an aporphine with 2 x OMe and OCH₂O substituents (11, 12). *P. acrochaetum* also yielded an alkaloid which gave a base peak at m/e 206 on the ms and with no observed M^+ , indicative of a 1-benzyltetrahydroisoquinoline or phthalideisoquinoline with 2 x MeO and NMe substituents in the AB rings; this alkaloid is also present in *P. curviscapum*. Another unidentified alkaloid from *P. curviscapum* gave M^+ 337 and ms fragmentation indicative of an aporphine alkaloid (11, 12).

The major alkaloids of *P. glaucum* in the literature are rhoeadine-types (1, 2). Two of the Iraqi samples contained rhoeadine-types as major alkaloids, whereas aporphines proved to be the major alkaloids of two other samples (table 1). The unidentified alkaloids from one sample of *P. glaucum* (S. Jasmin s.n.) had molecular ions at 323, 325 and 339 in their ms with fragmentation indicative of a series of related aporphines which differ in A and C ring substitution (11, 12).

Extracts from the two species of the section *Caratinae*, *P. macrostomum* and *P. bornmuelleri* were either weak or negative in their reactions to Dragendorff reagent. Over 50 g of one sample of *P. macrostomum* (A. Askari s.n.) was available and cheilanthifoline (19) and protopine (16) were isolated together with two unidentified alkaloids which are probably aporphines (M^+ 323 and 325) and an unidentified 1-benzyltetrahydroisoquinoline or phthalideisoquinoline (m/e 206, 100%). Previous investigations of *P. macrostomum* have yielded protopine, rhoeadine and papaverrubines A, B, D, E (1), and the papaverine-type alkaloids sevanine and macrostomine (13). No evidence was obtained for the presence of these latter two alkaloids which do have characteristic ms. The sample of Iraqi *P. macrostomum* which contained alkaloids was a low yielding strain, and

tlc showed that both the non-phenolic and phenolic fractions contained complex mixtures (table 1).

P. rhoeas, the common field poppy, a member of the section Orthorhoeades is very variable in its alkaloid content (9). Roemerine (5) and its proaporphine precursor mecambrine (1) were the major alkaloids of one of the five samples examined. Liriodenine (10), the corresponding oxoaporphine, was the major alkaloid of a second sample (table 1). In another sample of *P. rhoeas*, two unidentified alkaloids with ms showing the presence of molecular ions at *m/e* 337 and 339 and with fragmentation indicative of aporphines (11) were the major alkaloids. The same sample contained an unidentified phenolic alkaloid (*m/e* 192) indicative of a 1-benzyltetrahydroisoquinoline or phthalideisoquinoline with OMe, OH and NMe substituents in the AB rings. The only sample of *P. dubium* which was available yielded no alkaloids (table 1).

Three samples of *P. hybridum*, in the section Argemonorrhoeades, were examined and found to be generally weak or negative in their alkaloid reactions. The rhoeadine-type alkaloids glaucamine (14) and glaudine (15) were the major alkaloids of the roots of one sample (table 1). Berberine, coptisine, pahybrine, papaverrubines A, B, D, and sanguinarine have been reported from *P. hybridum* by previous investigators (1).

Three of the *Glaucium* species which are native to Iraq, *G. haussknechtii* Bornm., *G. cuneatum* Cullen, and *G. oxylum* Boiss. et Buhse, are rare (7) and were not available for chemical work. The remaining two species, *G. corniculatum* (L.) Rud. and *G. grandiflorum* Boiss. et Huet, are quite common and both were examined for their alkaloid content (table 1). The two subspecies of *G. carniculatum*, subspecies *corniculatum* and *refractum* (Nab.) Cullen and *G. grandiflorum* contained the same major alkaloids; allocryptopine (18) and protopine (16) were present in all of the samples and in all of the plant parts which were examined. Other alkaloids which were identified included corydine (6), isocorydine (7) and berberine (20); these three alkaloids have been reported previously from *Glaucium* species (1, 2). One sample of *G. corniculatum* (ld 41940) contained an unidentified alkaloid (M^+ 351, M^+-1 , M^+-15 , M^+-31) which was probably an aporphine (11, 12) and a phenolic alkaloid (M^+ 327, M^+-1 , M^+-15 , M^+-17 , M^+-31) which was probably an aporphine with 2 x OMe, 2 x OH and NMe substitution pattern. The presence of unidentified alkaloids in *P. grandiflorum* was also noted. Again, ms fragmentation is indicative of aporphines with molecular weights of 351 and 381.

Roemeria hybrida (L.) DC. and *R. refracta* DC., the latter being rare, are both native to Iraq (7). Two samples of *R. hybrida* were examined and tlc indicated that they both contained the same three alkaloids (table 1). The major alkaloid was identified as roehybrine (2).

Some 21 alkaloids have been identified, the presence of partially characterized and completely unidentified unknown alkaloids are indicated in some 18 papaveraceous species which were obtained without mounting expensive expeditions. The presence of different chemical strains of Iraqi species is shown for *P. persicum*, *P. glaucum*, and *P. rhoeas*. These results form a preliminary basis on which future alkaloid studies may be based when larger amounts of plant material become available, thus enabling identifications to be completed for the unidentified alkaloids listed in table 1. The findings illustrate the value of chemical investigations into herbarium material, particularly for those collections which are in excess of normal requirements.

EXPERIMENTAL²

PLANT MATERIAL.³—Thirty-six samples of 10 species of *Papaver*, 3 species of *Glaucium*, and 1 species of *Roemeria* were obtained mainly from herbarium sheets. The samples of plants which were extracted are listed in table 1.

EXTRACTION OF ALKALOIDS.—The dried, powdered plant material was macerated overnight with methanol and filtered; the marc was well washed with methanol. The combined methanol extracts and washings were concentrated to dryness under reduced pressure, and the residue was shaken with a 1:1 mixture of 3% sulfuric acid and chloroform. The separated aqueous acid extract was made alkaline with 10% ammonia and extracted with three successive quantities of chloroform. The combined chloroform extracts were shaken with three successive quantities of 5% sodium hydroxide to remove phenolic alkaloids. The chloroform extract was washed with water, separated, dried over anhydrous sodium sulfate and evaporated to dryness to yield *non-phenolic alkaloids*. The sodium hydroxide extract was made acidic with hydrochloric acid and then alkaline with 10% ammonia and extracted with three successive quantities of chloroform. The combined chloroform extracts were washed with water, separated, dried over anhydrous sodium sulfate and evaporated to dryness; the procedure yielded *phenolic alkaloids*. The yields of alkaloid obtained are given in table 1.

ALKALOID TESTS.—Non-phenolic and phenolic alkaloid extracts were each dissolved in 0.5 ml quantities of methanol. Ten μ l aliquots of each solution were applied to filter paper, dried and sprayed with Dragendorff's reagent. The intensity of orange spots produced was assessed visually by comparison with 5, 10, 20 and 30 μ l quantities of a solution of 0.25 mg codeine in 1 ml of methanol. The intensity of the orange colors produced was graded + to ++++ corresponding to the 5 μ l up to 30 μ l of standard solution of codeine. The results of the alkaloids tests are given in table 1.

THIN-LAYER CHROMATOGRAPHY (TLC).—Plates, 20 x 20 cm, were spread either with 0.25 mm of silica gel (for solvent systems A, B and E) or with alumina (for solvent systems C and D) and activated at 100° for 30 minutes. The following solvent systems were used for analytical and preparative chromatography: A. benzene-ethanol-conc. ammonia (80:20:0.3); B. benzene-acetone-methanol (7:2:1); C. *n*-heptane-diethylether-chloroform (4:1:5); D. chloroform-*n*-heptane (97.5:2.5); E. benzene-ethanol (9:1). Plates were sprayed with: (1) Dragendorff's reagent to reveal alkaloids as orange spots, and (2) 60% sulfuric acid, and heated at 110° for 5 minutes. The colors produced with this reagent have been described in a previous publication (6).

IDENTIFICATION OF ALKALOIDS—

Mecambrine (1)—identical tlc R_f values and ms with reference alkaloid (15).

Roehybrine (2)—identical ms with literature (16).

Floripavidine (3)—ms *m/e* (%) 427 (M^+ , 41), 281 (M^+ -146, 95), 280 (100), 266 (45), 250 (32), 238 (36); ¹H nmr (60 MHz, CDCl₃) δ 8.20 (1H, *m*; C-11 H), 7.20 (3H, *m*; C-8 H, C-9 H, C-10 H), 6.89 (1H, *s*; C-3 H), 5.41 (1H, *s*; C-1' H of rhamnose), 3.67 (3H, *s*; OMe), 2.54 (3H, *s*; NMe), 1.32 (3H, *d*, *J*=5Hz; C-5'CH₃ of rhamnose).

HYDROLYSIS.—Floripavidine (2 mg) was heated on a steam bath for 45 minutes in 6% hydrochloric acid (5 ml). The hydrolyzate was made alkaline with ammonium hydroxide and shaken with three successive portions of chloroform. The combined chloroform extracts were washed with a little water, dried over anhydrous sodium sulfate and evaporated to low volume. Tlc indicated the presence of one major alkaloid which had identical R_f values with *N*-methylasimilobine (4) (systems A and E).

N-methylasimilobine (4)—ms *m/e* (%) 281 (M^+ , 91), 280 (M^+ -1,100), 266 (M^+ -15, 43), 264 (M^+ -17, 33), 250 (M^+ -31, 60), 238 (M^+ -43, 37) (literature, 11); identical tlc R_f values with authentic sample.

Roemerine (5)—ms identical with literature (11); R_f values identical with reference alkaloid.

Corydine (6)—uv λ max (MeOH) 222, 265, 273, 308 nm; uv λ max (MeOH+NaOH) 232, 275, 338 nm, (literature, 11); ms, *m/e* (%) 341 (M^+ , 100), 340 (M^+ -1, 25), 326 (M^+ -15, 71), 324 (M^+ -17, 43), 310 (M^+ -31, 93) (literature, 11, 14); ¹H nmr (60 MHz, CDCl₃) δ 6.83 and 7.01 (2H, AB q, *J*=8 Hz; C-8H, C-9H), 6.70 (1H, *s*; C-3 H), 3.70 (3 H, *s*; C-11 OMe), 3.91 (6 H, *s*; C-2 and C-10 OMe), 2.54 (3H, *s*; NMe) (literature, 11).

²Uv spectra were obtained on a Perkin Elmer 402 spectrophotometer, and the ir spectrum on a SP 200 spectrophotometer. Ms were determined on an AEI MS 902 spectrometer at 70 eV and at inlet temperatures of between 180° and 225°. ¹H nmr spectra were obtained on a Perkin Elmer R 60 model R 12 A spectrometer at 60 MHz and on a Varian XL-100 spectrometer at 100 MHz. Chemical shifts are given in p.p.m. from tetramethylsilane which was used as the internal standard. Tlc adsorbents silica gel G and alumina G were obtained from E. Merck, Darmstadt, W. Germany.

³Herbarium samples were supplied by the Director of the National Herbarium of Iraq and the Director of the College of Agriculture, University of Baghdad, Iraq.

Isocorydine (7)—ms, *m/e* (%) 341 (M⁺, 52), 326 (M⁺-15, 100), 310 (M⁺-31, 60) (literature 11, 14); R_f values identical with reference alkaloid.

Roemerine N-oxide (8)—ms, *m/e* (%) 295 (M⁺, 7), 279 (M⁺-16, 56), 278 (100), 264 (32), 236 (85).

Dehydroroemerine (9)—ms *m/e* (%) 277 (M⁺, 100), 262 (9), 250 (13), 248 (11), 236 (20), 235 (26), 138.5 (M⁺⁺).

Liriodenine (10)—uv λ max (MeOH) 218, 273, 444 nm; uv λ max (MeOH+HCl) 253, 307, 408, 546 nm; ir (KBr) identical with literature (17); ¹H nmr (100 MHz, CDCl₃) δ 8.91 (1H, *d*, *J* = 5 Hz; C-5 H), 8.65 (1H, *m*, *J*_o = 7 Hz, *J*_m = 1.3 Hz; C-11 H), 8.61 (1H, *m*, *J*_o = 7 Hz, *J*_m = 2 Hz; C-8 H), 7.77 (1H, *d*, *J* = 5 Hz; C-4 H), 7.73 (1H, *m*, *J*_o = 7 Hz, *J*_m = 2 Hz; C-10 H), 7.61 (1H, *m*, *J*_o = 7 Hz, *J*_m = 1.3 Hz; C-9 H), 7.18 (1H, *s*; C-3H), 6.38 (2H, *s*; OCH₂O).

Alpinigenine (11)—ms identical with literature (18, 19), R_f values identical with alpinigenine isolated from *P. fugax* (6).

Rhoegenine (12), *Rhoeadine* (13), *Glaucamine* (14), *Glaudine* (15)—ms identical with literature (5) and R_f values identical with reference alkaloids.

Protopine (16), *Cryptopine* (17), *Allocriptopine* (18)—ms identical with literature (20) and R_f values identical with reference alkaloids.

Cheilanthifoline (19)—ms and R_f values identical with cheilanthifoline from *Fumaria judaica* (21).

Berberine (20)—ms, *m/e* (%) 336 (M⁺, 100), R_f values identical with reference alkaloid.

Narcotine (21)—identical ms and R_f values with reference alkaloid.

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