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ALKALOIDS OF TURKISH *PAPAVER TAURICOLA*

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Key Word Index – *Papaver tauricola*; Papaveraceae; alkaloids; rhoeadine-type.

Abstract—The major alkaloids of *Papaver tauricola* collected in three different parts of Anatolia have proved to be of the rhoeadine type. The three collections possessed different major alkaloids and the existence of chemical strains containing rhoeadine-type alkaloids, is indicated. In addition to the rhoeadine-type alkaloids (rhoeagenine, rhoeadine, oreogenine, oreodine, glaucamine, glaudine and epiglaudine), tetrahydroprotoberberine-(sinactine, scoulerine) and isopavine- (amurensinine) type alkaloids have been isolated as minor products. These findings contrast with the previous literature in which 1-benzyltetrahydroisoquinoline- and proaporphine types were reported to be the major alkaloids.

INTRODUCTION

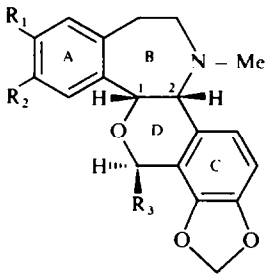
Papaver tauricola Boiss., cited by Cullen in the *Flora of Turkey*, is native to the screes and rocky slopes of Anatolia and it grows at an altitude of 1100–2800 m [1]. The ovate-globose capsules may be covered with long, white adpressed bristles from the bases of the capsules or the capsules may be glabrous [var. *leiocarpum* (Boiss.) Fedde]. The species, which occurs also in Northern Iraq and Iran, in Cullen's view, may possibly not be distinct from the Iranian *P. persicum* Lindl. [1]. Although Fedde in 1909 [2] clearly regarded *P. tauricola* and *P. persicum* as two distinct species, Cullen in *Flora Iranica* [3] listed *P. tauricola* as a synonym for *P. persicum*. Both names appear in the chemical literature because of their alkaloid contents but there appears to be no great differences between the two plants because armepavine and mecambrine have been identified as major alkaloids in both. The previous findings are summarised as follows: *P. persicum*: 1-benzyltetrahydroisoquinoline-(armepavine), proaporphine- (mecambrine, pronuciferine), aporphine-(mecambroline, nuciferine, *O*-demethylnuciferine, roemerine), protoberberine- (coptisine, palmatine), protopine-, benzophenanthridine- (sanguinarine), papaverrubine-type alkaloids; *P. tauricola*: 1-benzyltetrahydroisoquinoline- (armepavine), proaporphine- (mecambrine), aporphine- (nuciferine), benzophenanthridine-(sanguinarine), papaverrubine-type alkaloids [4–7].

In a preliminary short communication [8], as part of the present investigation, it was reported that the rhoeadine-type alkaloids, rhoeadine and oreodine, were the major alkaloids in a Turkish sample of *P. tauricola*. In the present communication, the work is extended to include the identification of other alkaloids and the investigation of two other collections of *P. tauricola* from other parts of Anatolia.

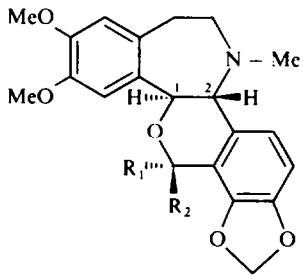
RESULTS AND DISCUSSION

The major alkaloids of three different collections of *P. tauricola* from Anatolia were of the rhoeadine type. Plants collected in Malatya contained the *cis* B/D-ring with A-ring dimethoxy substituted alkaloids, oreogenine (**4**) and oreodine (**5**) with the corresponding A-ring methylenedioxy analogues, rhoeagenine (**1**) and rhoeadine (**2**) as minor alkaloids. Other minor alkaloids were sinactine (**10**) and scoulerine (**11**), which have been shown to be precursors of rhoeadine-type alkaloids in *P. rhoeas* [9]. The isopavine-type alkaloid, amurensinine (**12**), which has not previously been known as a type of alkaloid in the section *Miltantha*, was also a minor constituent. Two distinct forms of *P. tauricola* were present in the Malatya samples as shown by the capsules, which were either glabrous or covered with white adpressed bristles ('hairy capsules'). Both types of capsule contained identical major alkaloids. From Kayseri plants, the major alkaloids were found to have *trans* B/D-ring junctions with dimethoxy substituted A-rings, glaucamine (**7**), glaudine (**8**) and epiglaudine (**9**) although rhoeagenine (**1**) with a *cis* B/D-ring junction was also present. Rhoeagenine (**1**) was the major alkaloid of plants obtained from Gulek. These findings differ from those of other workers who have obtained alkaloids from *P. tauricola* [4–7] (see Introduction). Rhoeadine-type alkaloids are commonly found in species of *Papaver* but it is surprising to find them as the major alkaloids in *P. tauricola* since previously this species has yielded 1-benzyltetrahydroisoquinoline-, proaporphine- and aporphine-type alkaloids. These findings provide a further example in which a Turkish species of *Papaver* has proved to contain different major alkaloids from those reported in the literature; see for example the alkaloids of *P. fugax* [10] and of *P. pseudo-orientale* [11]. The other unexpected result is that the three samples of *P. tauricola*, which were all collected at the fruiting stage, contained three different groups of major alkaloids. It appears that there are three chemical strains which possess rhoeadine-type alkaloids.

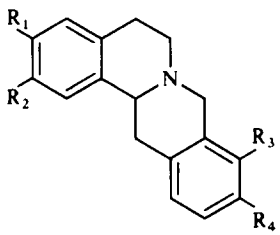
The initial extractions carried out on the three different samples utilised normal extraction procedures which would readily have yielded the anticipated 1-benzyltetrahydroisoquinoline-, proaporphine- and aporphine-type alkaloids but the major alkaloids proved to be of the



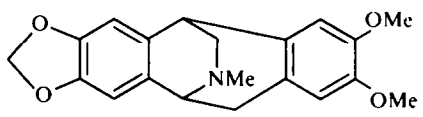
	R_1	R_2	R_3
1	$-OCH_2O-$		OH
2	OCH_2O		OMe
3	$-OCH_2O-$		OEt
4	OMe	OMe	OH
5	OMe	OMe	OMe
6	OMe	OMe	OEt



	R_1	R_2
7	OH	H
8	H	OMe
9	OMe	H



	R_1	R_2	R_3	R_4
10	OMe	OMe	OCH_2O	
11	OMe	OH	OH	OMe



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rhoeadine type. It is known that such alkaloids can undergo chemical changes, especially when treated with mineral acid [12, 13]. Glaudine (**8**) or epiglaudine (**9**) on treating with 0.1 N HCl for 10–30 sec in boiling water, yield glaucamine (**7**). Under more rigorous conditions, glaudine or epiglaudine in N HCl for 1 hr in boiling water yield oreogenine (**4**) in which there has been a change in configuration from B/D *trans* to *cis*. Thus it is advisable to avoid use of mineral acid during extraction and isolation procedures. Since it was not easy to repeat the isolation of alkaloids from all three samples of *P. tauricola*, it was decided to check whether or not the alkaloids obtained from the Malatya sample were natural products or were obtained by chemical transformations due to isolation procedures. Acetic acid (3%) was used instead of mineral acid and two extraction procedures were compared. The use of ether/ammonia for initial extraction resulted in cleaner alkaloid extracts than when ethanol was used. Initial ethanol extraction yielded oreogenine (**4**) as the major alkaloid, whereas ether extraction yielded oreodine (**5**) as the major alkaloid. The most likely explanation for these differences is that ether failed to extract the more polar oreogenine which was extracted by the ethanol procedure. Apart from the differences in oreodine/oreogenine proportions, the other alkaloids were identical with those isolated in the initial work. The isolation of *O*-ethyloreogenine (**6**) from extracts of Malatya samples and of *O*-ethylrhoeagenine (**3**) from Kayseri and Gulek samples can be discounted, however, since it is highly probable that the 14-ethoxy compounds were formed from ethanol/H^+ during isolation procedures.

The identities of the tetrahydroprotoberberine alkaloids sinactoine (**10**) were based on comparable MS [14] and ^{1}H NMR data and of scoulerine (**11**) on MS data [15]. Amurensinine (**12**), the isopavine alkaloid, was also readily identified by its characteristic MS [16]. Not all of the rhoeadine-type alkaloids which are theoretically possible as natural products have yet been isolated. Hence, in view of the number of closely related compounds, it is necessary to use a combination of MS and ^{1}H NMR for identifications. MS gave a distinct M^+ for all of the rhoeadine-type alkaloids isolated and further fragmentation indicated the nature of the substituents in the A and D-rings for the acetals (**2, 3, 5, 6, 8, 9**) and for the hemiacetals (**1, 4, 7**) [17, 18]. MS does not, however, reveal the stereochemistry of the B/D-rings and it is necessary to resort to ^{1}H NMR spectroscopy. The coupling constants for the protons on C-1 and C-2 are in the order of 2 Hz for alkaloids with a *cis* B/D-ring junction whereas the *trans* B/D alkaloids give rise to spectra with a coupling constant of *ca* 9 Hz [13, 19–21]. The question of the configuration of the natural products at C-14 is not so clear-cut because mutarotation readily occurs. The absolute configuration of the C-14 hydroxyl in rhoagenine

has been stated to be β [22] but recently it has been proposed that rhoeagenine possesses a C-14 hydroxyl with an α-configuration [23]. The results obtained from X-ray crystallographic studies depend upon crystals in which the hydroxyl has the preferred configuration.

It is interesting to note the similarity between the alkaloids of *P. tauricola* reported in this communication and those of *P. rhoeas* (rhoeadine, rhoeagenine, glaucamine, glaudine, sinactine) [24]. Rhoeadine-type alkaloids have not been reported previously as major constituents of species from the section *Miltantha*, but they are the major alkaloids of species from the sections *Orthorhoeades* (*P. arenarium*, *P. commutatum*, *P. dubium*, *P. strigosum*, *P. rhoeas*), *Pilosa* (*P. atlanticum*, *P. oreophilum*, *P. pilosum*), *Mecones* (*P. glaucum*), *Scapiflora* (*P. nudicaule*) and *Argemonorhoeades* (*P. argemone*) [13].

EXPERIMENTAL

Plant material. The plants were collected in Anatolia by A. Baytop, E. Tuzlaci and G. Sariyar during 1977. Identification was made by Professor A. Baytop and reference samples are retained in the herbarium of the Faculty of Pharmacy, Istanbul University. The three collections examined were ISTE 37 683, collected between Bünyan and Pinabasi at Ekrek village near to Kayseri on slopes at 1400 m, 21 June 1977; ISTE 37 755, collected between Darende and Malatya, 80 km from Malatya at 1600 m, 22 June 1977; ISTE 37 846, collected at the Gulek Pass at 1050 m, 25 June 1977.

TLC. The adsorbents used were Si gel G (Merck) and Al_2O_3 G (Merck). The solvent systems were A. Si gel: C_6H_6–Me_2CO–conc NH_4OH (80:20:0.1); B. Si gel: C_6H_6–Me_2CO–conc NH_4OH (90:10:1); C. Si gel: nC_7H_{16} $CHCl_3$–EtOH (5:3:2), D. Al_2O_3: nC_7H_{16}–$CHCl_3$–Et_2O (5:3:2); E. Al_2O_3: nC_7H_{16}–$CHCl_3$–Et_2O (4:5:1), F. Al_2O_3: nC_7H_{16}–CH_2Cl_2–Et_2O (5:3:2).

Isolation of alkaloids. 1. *Malatya sample.* (a) Dried, powdered aerial parts (leaves, stems, capsules, 775 g) were extracted with EtOH in a Soxhlet extractor for 24 hr. The EtOH extract was concd under red. pres. and the residue extracted with 3% H_2SO_4 until negative to Dragendorff reagent. The acid extract was washed with Et_2O, made alkaline with NH_4OH and extracted successively with $CHCl_3$. The combined $CHCl_3$ extracts were shaken with 5% NaOH to remove phenolic alkaloids. The $CHCl_3$ was washed with H_2O, dried (Na_2SO_4) and concd to dryness under red. pres. to yield 5.54 g (0.71%) total non-phenolic alkaloid. Initial separation was obtained on an Al_2O_3 (neutral) column (Merck) 30 × 2.5 cm and elution with nC_7H_{16}–Et_2O–$CHCl_3$ (5:5:1), 60 × 10 ml fractions collected, then with $CHCl_3$, 60 × 10 ml fractions collected. Like fractions were combined on the basis of their similarities on TLC to yield ethyl rhoeagenine (20 mg) from fractions 25–41. The $CHCl_3$ fractions were combined (1.26 g) and an aliquot (0.32 g) separated on prep. TLC (system A) to yield rhoeagenine (24 mg) and oreogenine (155 mg). (b) Hairy capsules (dried, powdered, 100 g) were moistened with 10% NH_4OH and macerated with Et_2O for 24 hr. The filtered Et_2O extract was shaken with 3% H_2SO_4 until no alkaloid remained in the Et_2O. The combined acid extracts were made alkaline with NH_4OH, extracted with Et_2O and phenolic alkaloids removed by shaking with 5% NaOH. The Et_2O extract was washed, dried and concd to dryness under red. pres. to yield 0.76 g (0.76%) total crude non-phenolic alkaloid. Oreodine (0.51 g) was obtained as colourless crystals from Et_2O. A combination of prep. TLC (systems B, D, E) of the mother liquor yielded rhoeadine (30 mg) crystallized from Me_2CO–C_6H_6, oreodine (28 mg) crystallized from Me_2CO–C_6H_6, sinactine (30 mg) and amurensinine (6 mg). The NaOH extract was made acidic with HCl, alkaline with NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ extract was washed, dried, concd to dryness under red. pres. to yield phenolic alkaloid, 28 mg (0.03%). Prep. TLC (system A) yielded scoulerine (10 mg). (c) Non-hairy capsules (50 g) were extracted by the method described in (b) above to yield 0.6 g (1.2%) non-phenolic alkaloids and 0.01 g (0.02%) phenolic alkaloids. TLC indicated both fractions were identical in composition to the alkaloids present in the hairy capsules. (d) Comparison of extraction procedures: (i) Dried powdered plant material extracted by method (b) above but substituting 3% HOAc for 3% H_2SO_4; (ii) Dried powdered plant material was macerated with EtOH for 24 hr, filtered, concd to dryness under red. pres. The residue was extracted with 3% HOAc (3 ×), the combined acid extracts washed with Et_2O, made alkaline with NH_4OH and extracted with $CHCl_3$ (3 ×). The combined $CHCl_3$ extracts were washed, dried and concd to dryness under red press. Non-hairy capsules (0.5 g), method (i), 4.5 mg white residue; method (ii) 4.2 mg yellow residue. Leaves and stems of same plants (9.4 g), method (i) 57 mg white residue; method (ii) 60 mg yellow residue. TLC (systems B, C, F) indicated that the alkaloids of the capsules were identical with those of the leaves and stems. Methods (i) and (ii) yielded extracts in which TLC indicated the presence of rhoeadine, oreodine, rhoeagenine and oreogenine. In method (i) oreogenine was a minor component but in method (ii) it was a major component.

2. *Kayseri sample.* (a) Dried powdered aerial parts (leaves, stems, capsules, 150 g) were extracted as described for 1(b) to yield total non-phenolic alkaloid, 1.08 g (0.72%). An aliquot (0.37 g) was separated by prep. TLC (system D) to yield glaudine (9 mg) and ethylrhoeagenine (6 mg). Prep. TLC (system A) yielded rhoeagenine (17 mg) and glaucamine (25 mg). (b) Dried, powdered aerial parts (leaves, stems, capsules, 450 g) were extracted by maceration in MeOH and the alkaloids isolated as described in 1(a) to yield total non-phenolic fraction, 3.22 g (0.71%) and total phenolic fraction, 0.23 g (0.05%). An aliquot (2.95 g) of the non-phenolic fraction was separated on an Al_2O_3 column (neutral, Merck, 30 × 2.5 cm) which was eluted with nC_7H_{16}–Et_2O–$CHCl_3$ (5:5:1) and 20 × 10 ml fractions collected. Fractions 10–12 yielded 328 mg alkaloid which was separated by prep. TLC (system D) to yield epiglaudine (58 mg) and glaudine (49 mg).

3. *Gulek sample.* (a) Dried powdered capsules (20 g) were extracted as for 2(b) to yield 0.61 g (3.1%) total crude alkaloid. Elution with nC_7H_{16}–Et_2O–$CHCl_3$ (5:5:1) from an Al_2O_3 column (neutral, Merck) yielded ethyl rhoeagenine (69 mg). (b) Dried powdered aerial parts (leaves, stems, capsules, 55 g) were extracted as for 2(b) to yield 574 mg (1.0%) total crude alkaloid. A combination of column chromatography as for 3(a) and prep. TLC (system A) yielded rhoeagenine (13 mg).

Identification of alkaloids. Rhoeagenine (**1**). ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 4.56 (1 H, *br s*, C-1), 3.13 (1 *H*, *br s*, C-2); 6.13 (1 H, *s*, C-14), 6.65 (2 H, *s*, C-6, C-9), 6.72 (2 H, *s*, C-10, C-11); 2.20 (3 H, *s*, NMe), 5.92 (2 H, *s*, A-ring OCH_2O), 5.95 and 6.13 (2 H, *dd*, J = 1.3 Hz, D-ring OCH_2O). MS *m/e* (rel. int.): 369 (11, M^+), 314 (4), 311 (2), 206 (100), 192 (64), 177 (11), 163 (96) [17, 18]. *Rhoeadine* (**2**). ^{1}H NMR ($CDCl_3$): δ 5.05 (1 H, *d*, $J_{1,2}$ = 2 Hz, C-1). 3.61 (1 H, *d*, $J_{1,2}$ = 2 Hz, C-2), 5.76 (1 H, *s*, C-14), 6.65 (1 H, *s*, C-6), 6.75 (1 H, *s*, C-9), 6.80 (2 H, *s*, C-10, -11), 2.33 (3 H, *s*, NMe), 3.55 (3 H, *s*, C-14 OMe), 5.94 (2 H, *s*, A-ring OCH_2O), 5.97 and 6.10 (2 H, *dd*, J = 2 Hz, D-ring OCH_2O) [13]. MS *m/e* (rel. int.): 383 (50, M^+), 368 (50), 352 (14), 206 (50), 192 (36), 190 (28), 177 (100), 163 (50), [17, 18]' Identical R_f values in systems A and B with authentic sample. *Ethylrhoeagenine* (**3**) ^{1}H NMR ($CDCl_3$): δ

5.08 (1 H, *d*, $J_{1,2}$ = 2 Hz, C-1), 3.62 (1 H, *d*, $J_{1,2}$ = 2 Hz, C-2), 5.88 (1 H, *s*, C-14), 6.63 (1 H, *s*, C-6 H), 6.73 (1 H, *s*, C-9 H), 6.77 (2 H, *s*, C-10, C-11), 2.31 (3 H, *s*, NMe), 1.29 (3 H, *t*, *J* = 6 Hz; C-14 OEt), 5.94 (2 H, *s*, A-ring OCH_2O), 5.98 and 6.10 (2 H, *dd*, *J* = 1.3 Hz, D-ring OCH_2O). MS *m/e* (rel. int.): 397 (50, M^+), 368 (83, M^+ − Et), 352 (20, M^+ − OEt), 192 (16), 190 (20), 177 (100), 163 (16) [18]. *Oreogenine* (**4**). ^{1}H NMR ($CDCl_3$): δ 4.62 (1 H, *br s*, C-1), 3.18 (1 H, *br s*, C-2), 6.16 (1 H, *s*, C-14), 6.68 (4 H, *s*, C-6, C-9, C-10, C-11), 2.21 (3 H, *s*, NMe); 6.02 (2 H, *s*, D ring OCH_2O); 3.80 and 3.88 (2 × 3 H, *s*, A-ring OMe). MS *m/e* (rel. int.): 385 (18, M^+), 370 (22), 354 (11), 209 (11), 206 (11), 193 (22), 179 (22), 148 (100) [18]. *Oreodine* (**5**). ^{1}H NMR ($CDCl_3$): δ 5.05 (1 H, *d*, $J_{1,2}$ = 2 Hz, C-1); 3.67 (1 H, *d*, $J_{1,2}$ = 2 Hz, C-2); 5.74 (1 H, *s*, C-14); 6.65 (1 H, *s*, C-6); 6.78 (3 H, *s*, C-9, C-10, C-11); 2.32 (3 H, *s*, NMe); 3.55 (3 H, *s*, C-14 OMe); 5.95 and 6.08 (2 H, *dd*, *J* = 1.3 Hz, D-ring OCH_2O), 3.82 and 3.87 (2 × 3 H *s*, A-ring MeO) [13, 21]. MS *m/e* (rel. int.): 399 (83, M^+), 384 (72), 368 (20), 356 (7), 206 (37), 193 (100), 178 (8), 175 (10) [18]. *Ethyloreogenine* (**6**). ^{1}H NMR ($CDCl_3$): δ 5.13 (1 H, *d*, $J_{1,2}$ = 2 Hz, C-1), 3.70 (1 H, *d*, $J_{1,2}$ = 2 Hz, C-2), 5.89 (1 H, *s*, C-14) 6.70 (1 H, *s*, C-6), 6.80 (3 H, *s*, C-9, C-10, C-11), 2.32 (3 H, *s*, NMe), 1.30 (3 H, *t*, *J* = 6 Hz, C-14 OEt), 5.89 and 6.05 (2 H, *dd*, *J* = 1.3 Hz), D-ring OCH_2O), 3.82 and 3.89 (2 × 3 H *s*, A-ring OMe). MS *m/e* (rel. int.): 413 (74, M^+), 384 (80, M^+ − Et), 234 (6), 220 (35), 206 (11), 193 (100). *Glaucamine* (**7**). ^{1}H NMR (DMSO-d_6): δ 5.68 (1 H, *d*, $J_{1,2}$ = 9 Hz, C-1), 3.80 (1 H, *d*, $J_{1,2}$ = 9 Hz, C-2), 6.08 (1 H, *s*, C-14), 6.80 (1 H, *s*, C-6), δ 7.13 (1 H, *s*, C-9), 6.87 (2 H, *s*, C-10, C-11), 2.25 (3 H, *s*, NMe), 6.01 and 6.08 (2 H, *br s*, *D*-ring OCH_2O), 3.70 and 3.73 (2 × 3 H, *s*, A-ring 2 × OMe) [13, 21]. MS *m/e* (rel. int.): 385 (100, M^+), 370 (20), 354 (10), 209 (12), 206 (12), 193 (24), 179 (23), 148 (100) [18]. Identical R_f values in systems A and B with authentic sample. *Glaudine* (**8**). ^{1}H NMR ($CDCl_3$): δ 5.21 (2 H, *d*, $J_{1,2}$ = 9 Hz, C-1), 4.10 (1 H, *d*, $J_{1,2}$ = 9 Hz, C-2), 5.78 (1 H, *s*, C-14), 6.69 (1 H, *s*, C-6), 7.37 (1 H, *s*, C-9), 6.81 and 7.08 (2 H, ABq, *J* = 8 Hz, C-10, C-11), 2.26 (3 H, *s*, NMe), 3.70 (3 H, *s*, C-14 OMe), 5.94 and 6.05 (2 H, *dd*, *J* = 1.3 Hz, D-ring OCH_2O); 3.89 (6 H, *s*, A-ring 2 × OMe) [20]. MS *m/e* (rel. int.): 399 (73, M^+), 384 (80), 220 (4), 206 (34), 193 (100), 192 (12). Identical R_f values in systems A and B with authentic sample. *Epiglaudine* (**9**). ^{1}H NMR ($CDCl_3$): δ 5.56 (1 H, *d*, $J_{1,2}$ = 9 Hz, C-1), 4.04 (1 H, *d*, $J_{1,2}$ = 9 Hz, C-2), 5.75 (1 H, *s*, C-14); 6.69 (1 H, *s*, C-6), 7.31 (1 H, *s*, C-9), 6.78 and 7.08 (2 H, ABq, *J* = 8 Hz, C-10, C-11), 2.32 (3 H, *s*, NMe); 3.58 (3 H, *s*, C-14 OMe), 5.98 and 6.05 (2 H, *dd*, *J* = 1.3 Hz, D-ring OCH_2O), 3.89 (6 H, *s*, A-ring 2 × OMe) [13, 20, 21]. MS *m/e* (rel. int.): 399 (73, M^+), 384 (80), 220 (4), 206 (34), 193 (100), 192 (12). *Sinactine* (**10**). ^{1}H NMR ($CDCl_3$): δ 3.85 and 3.87 (2 × 3 H, *s*, 2 × OMe), 5.92 (2H, *br s*, OCH_2O), 6.68 (4 H, *m*, C-1, C-4, C-11, C-12). MS, *m/e* (rel. int.): 339 (29, M^+), 338 (20), 324 (2), 322 (1), 190 (13), 149 (14), 148 (100). *Scoulerine* (**11**). MS *m/e* (rel. int.): 327 (74, M^+), 326 (44), 312 (9), 310 (9), 206 (26), 192 (22), 178 (100), 176 (31), 163 (27), 150 (65), 135 (23) [15]. *Amurensinine* (**12**). MS *m/e* (rel. int.): 339 (20, M^+), 338 (19), 312 (4, M^+, −17), 296 (27), 188 (100) [16].

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