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ALKALOIDS FROM *GLAUCIUM GRANDIFLORUM* VAR.*GRANDIFLORUM*

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SUMMARY

Six alkaloids, allocryptopine, corydine, isocorydine, isocorytuberine, N-methylcanadine and protopine have been isolated from two samples of *Glaucium grandiflorum* Boiss. et Huet var. *grandiflorum* collected from Bolu and Sivas.

ÖZET

İki farklı yörede,Bolu ve Sivas'da yetişen *Glaucium grandiflorum* Boiss. et Huet var. *grandiflorum* bitkisinden altı alkaloit,allocryptopine, corydine, isocorydine, isocorytuberine, N-methylcanadine ve protopine elde edildi.

Key Words:*Glaucium grandiflorum* var.*grandiflorum*, isoquinoline alkaloids.

INTRODUCTION

In the Flora of Turkey, *Glaucium grandiflorum* has two varieties, var.*grandiflorum* and var. *torquatum*, of which the latter is an endemic one.

Attention has long been paid to *Glaucium* species for their glaucine content since this alkaloit is known to have an antitussive property.

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Previous studies on the alkaloids of some Turkish *Glaucium* species have shown the presence of glaucine as a major alkaloit. However among them *G.grandiflorum var.torquatum* has been found to contain this alkaloit only as a minor one [2,4].

Besides glaucine, the other alkaloids isolated from *G.grandiflorum* were reported to be aporphine (glauvine, isoboldine, isocorydine, oxoglaucine and thalicmidine), protoberberine (berberine, tetrahydrojatrorrhizine, tetrahydropalmatine), protopine (allocryptopine, protopine) and benzophenanthridine (-8-acetonyldihydrochelerythrine, dihydrochelerythrine, norchelidonine, and sanguinarine) types [5,7].

RESULTS AND DISCUSSION

In this work, the alkaloids of Turkish *Glaucium grandiflorum* var.*grandiflorum* have been studied for the first time. Two alkaloids, isocorydine and protopine, have been isolated from both of the samples collected from Bolu (I) and Sivas (II) as major alkaloids. The minor alkaloids were aporphine types isocorytuberine and corydine in sample I and allocryptopine and N-methylcanadine in sample II. The presence of isocorytuberine (aporphine type) has been shown in *G.grandiflorum* for the first time.

This result shows that the two samples of *G.grandiflorum* var. *grandiflorum* have similarities in their major alkaloit content. But they have different minor alkaloids. Neither of them yielded glaucine. The structure of the alkaloids were identified by spectroscopic means and by TLC comparison.

EXPERIMENTAL

Material: The plant material was collected at the flowering stage from Bolu (Gerede) (sample I) in July 1997 and from Sivas (sample II) in June 1995. Voucher specimens (sample I: ISTE 74322, sample II: ISTE 68159) are retained at the Faculty of Pharmacy, Istanbul University. Total tertiary alkaloids (17.2 g and 1.9 g) were obtained from the aerial parts of sample I (2500 g) and sample II (355 g) following the reported methods [8].

Separation of alkaloids: Sample I: Isocorydine (6.8 g), corydine (0.3 g) and protopine (1.5 g) were obtained by column chromatography on silicagel

(Kieselgel 60, Korngrösse 0.063-0.2 mm) eluting with $CHCl_3$, $CHCl_3$:MeOH (9:1). Fractions of 25 ml were collected. Preparative TLC was then used for further separation and purification on silicagel with the system $CHCl_3$:MeOH (8:2) obtaining 30 mg of isocorytuberine. Sample II: The alkaloids of this sample were also separated by column chromatography as described for sample I. Isocorydine (0.38 g) and protopine (0.23 g) were obtained. Allocryptopine (0.039 g) and N-methylcanadine (0.018 g) were separated by preparative TLC on silicagel using systems C_6H_6:$(CH_3)_2CO$:$(C_2H_5)_2O$: %25 NH_4OH (40:60:10:3) and $CHCl_3$:MeOH (9:1) respectively.

Corydine crystallized from MeOH, m.p. 140 °C, UV λ_{max}^{MeOH} 222, 264, 270, 304 nm (1,2,10,11 substituted aporphines), ^{1}H-NMR (200 MHz, $CDCl_3$), 2.56 (3H, s, N-CH_3), 3.73 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 6.69 (1H, s, H-3), 7.07 and 7.09 (2H, d, J:8 Hz, H-8 and H-9).

Isocorytuberine UV λ_{max}^{MeOH} 220, 273, 308 nm, ^{1} H-NMR (200 MHz, $CDCl_3$) δ 2.56 (3H, s, N-CH_3), 3.70 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 6.71 (1H, s, H-3), 6.93 and 7.3 (2H, d, J:8Hz, H-8 and H-9).

N-methylcanadine UV λ_{max}^{MeOH} 216, 286 nm, ^{1} H-NMR (200MHz, $CDCl_3$) δ3.04 (3H, s, N-CH_3), 3.87 (3H, s, OCH_3), 3.95 (3H, s, OCH_3), 5.99 (2H, s, OCH_3), 5.99 (2H, s, O-CH_2-O), 6.70 (1H, s, H-1), 6.76 (1H, s, H-4), 6.94 and 7.01 (2H, d, J:8 Hz, H-10 and H-11). UV and ^{1}H-NMR spectra of the above three alkaloids were consistent with literature values (3,9,10).

The other alkaloids (allocryptopine, protopine and isocorydine) were determined by direct comparison. (UV, IR, ^{1}H-NMR and TLC) with authentic samples.

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