

MARRUBIUM PARVIFLORUM'DA FLAVON VE TERPENLER

TERPENOIDS AND A FLAVONE FROM MARRUBIUM PARVIFLORUM

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SUMMARY

Marrubium Parviflorum Fisch. et Mey. subsp. *oligodon* (Boiss.) Seybold (Labiatae) was investigated for its terpenoids and flavonoidal compounds. β - Sitosterol, α - amirin and apigenin-7-O-glucoside have been isolated and identified by spectral methods.

ÖZET

Marrubium Parviflorum Fisch. et Mey. Subsp. *oligodon* (Boiss.) Seybold (Labiatae) bitkisi, terpenoid ve flavonoid bileşikleri yönünden incelenmiştir. β -Sitositerol, α - amirin ve apigenin-7-O-glukozid bileşikleri izole edilerek, spektral yöntemlerle yapıları aydınlatılmıştır.

INTRODUCTION

The plant is distributed mainly in central Anatolia. The plant is apparently endemic for Turkey (1). The plant is erect, prennial, the stems are 20-70 cm, stellate-pilose, usually dense. Basal leaves very small densely white pilose, cauline leaves petiolate. Calyx teekt (5-8), unequal when more then 5. Verticillasters several-flowered. Corolla is white.

EXPERIMENTAL

The plant was collected from Eskişehir (Oğlakçı Köyü) in 1983, a voucher is deposited in the Herbarium of Faculty of Pharmacy, Univ. of Istanbul (ISTE 50866). Dried and powdered plant (680g) was macerated with acetone. After filtration, it was extracted with ethanol in a

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Soxhlet. A silicagel column was used to fractionate the acetone extract. The elution started with benzene, increasing amounts of chloroform were added and the elution completed with ethanol. β -Sitosterol and α -amyrin were obtained from acetone extract and cleaned by preparative thin layer chromatography. The identification of these compounds were done by comparing their spectral data to those of known compounds as well as by thin layer chromatographic comparison with authentic samples.

The alcohol concentrate of *Marrubium parviflorum* (oligodon) was reextracted with ethylacetate to obtain the flavonoidal compounds. A polyclar (Gaf Corporation) column (5x50 cm) was used for separation. Chloroform-ethanol (2:1) mixture was used to elute the column, by reducing the amount of chloroform.

One flavonoid was obtained from this column and it was cleaned from Sephadex LH-20 column (2x15) by eluting with MeOH. The fractions were checked on cellulose TLC plates. The similar fractions were combined. The purified flavonoid was identified by UV spectra and by UV shifts using MeOH, NaOMe, AlCl_3 , AlCl_3/HCl , NaOAc, NaOAc/ H_3BO_3 , as well as by comparing with an authentic sample, by acid hydrolysis (apigenin and glucose).

RESULT AND DISCUSSION

β -Sitosterol: IR (in KBr) showed the bands at 3400 cm^{-1} (OH), at 2900 and 2850 cm^{-1} (aliphatic C-H), at 1660 , 1640 and 1600 cm^{-1} (double band), characteristic divided bands at 1450 and 1380 cm^{-1} (isopropyl group at the side chain).

NMR spectrum showed CH_3 - 18 and CH_3 - 19 at $0.78\ \delta$ (6H singlet), CH_3 -21 at $0.82\ \delta$ (3H doublet), OH group at $1.65\ \delta$ as shown by D_2O exchange. Vinylic hydrogen at $5.3\ \delta$ (1H multiplet), hydrogen next to hydroxyl group is at $3.65\ \delta$, other bands are between 0.82 - $1.65\ \delta$ ppm.

Acetylation of the compound was carried out with 100 mg of K, in the usual way. The m.p. of the acetyl derivative was 169°C , analytical calculations for $\text{C}_{31}\text{H}_{52}\text{O}_2$, C, 81.6; H, 11.5 %. Found, C, 81.77; H, 11.2%. In IR spectrum instead of OH band there was acetyl carbonyl at 1730 cm^{-1} , other acetyl bands were observed at 1360 , 1250 cm^{-1} . In NMR spectrum the acetyl band was seen at $2.00\ \delta$ whereas OH band disappeared. The hydrogen next to hydroxyl group shifted to $4.8\ \delta$ ppm.

∞ -**Amyrin**: IR spectrum showed the bands at 950, 1025, 1245, 1365, 1450, 2965 cm^{-1} and the hydroxly group at 3450 cm^{-1} .

NMR spectrum gave the methly dublets and the singlets between 0,6-1.8 ppm indicating an ursane type compound. The vinylic proton at 5.2 ppm (+, 1H). The proton adjacent to the hydroxyl is at 3.7 ppm.

Apigenin-7-0-glucoside: Chromatographic Data:

Spot Appearance : (UV) deep purple
(UV/ NH_3) yellow-green

Rf Values: 0,61 (TBA), 0,23 (HOAc)

UV Spectral Data (λ_{max} , nm) :

MeOH 268, 333; NaOMe 245 sh, 269, 301 sh, 386; AlCl_3 276, 300, 348, 386; AlCl_3/HCl 277, 299, 341, 382; NaOAc 256 sh, 267, 355, 387; NaOAc/ H_3BO_3 267, 340.

REFERENCE

1. CULLEN, J.: Marrubium L. in Davis, P.H. (ed.), *Flora of Turkey and the East Aegean Islands*, Edinburgh, Edinburgh University Press, 7, 165 - 178 (1982).

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