Alquds, a New Flavone Glycoside from *Calamintha incana*

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Alquds, *Calamintha incana*, Lamiaceae

Alquds, a new flavone glycoside was isolated from the aerial parts of *Calamintha incana* and identified on the basis of spectral data (1- and 2-D NMR, IR, UV) and comparative study.

Introduction

*Calamintha* (Lamiaceae) contained about 100 species of aromatic herbs or shrubs distributed in temperate region and tropical mountain [1]. Previous phytochemical study of this genus shows the presence of eursolic acid (triterpenoid) and its derivatives [2, 3] as well as flavonoids and tannins [4]. This communication describes the isolation and structure elucidation of alquds, a new flavone glycoside from *Calamintha incana*.

Results and Discussion

Alquds was isolated as a white powder from the fraction obtained as a result of VLC of the methanolic extract with 20% MeOH/CHCl₃.

The UV spectrum showed intense absorption bands at λ_max (MeOH) at 264.2 and 332.6 nm. The IR spectrum (KBr) exhibited absorptions at 3475–3200 and 1660 cm⁻¹ corresponding to hydroxyl and carbonyl functions. The positive-ion FAB mass spectrum exhibited the molecular ion peak at m/z 593 [M+H]⁺. The same spectrum also showed the fragment ions at m/z 447 [(M+H)-rhm]⁺ and 285 [(M+H)-(glc+rhm)]⁺.

The 13C NMR spectrum showed the presence of 26 signals which were resolved through DEPT experiment as two methyls, a methylene, fifteen methine and eight quaternary carbons. Some chemical shift values in 13C NMR spectrum indicated the presence of two sugar units. The proton at δ 5.05 appeared as a doublet (J = 7.3 Hz) correlated to the carbon at δ 99.9 showed the presence of glucose moiety in the molecule. The down field shift of methylene in glucose about 5.5 ppm [5] indicated the attachment of second sugar unit to it. The second sugar unit was considered as rhamnose due to the appearance of signals at δ 4.55 (1H, 1H, J = 6.2 Hz, H-6") and 1.07 (3H, d, J = 6.2 Hz, H-6"). The attachment of rhamnose to methylene of glucose was confirmed by the HMBC interaction of anomeric proton at δ 4.55 (H-1") to methylene carbon (C-6").

A signal having two protons integration in the 1H NMR spectrum at δ 8.04 appeared as a doublet with 8.9 Hz coupling constant. A similar type of doublet also appeared at δ 7.14. The same value of coupling constant (8.9 Hz) and mutual interaction in the cosy-45° experiment of these protons revealed their ortho couping in ring B of flavones [6].

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The chemical shift $\delta$ 8.04 was assigned to H-2' and H-6' due to their HMBC interaction with the quaternary carbon at $\delta$ 164.6 (C-2). The chemical shift $\delta$ 7.14 was automatically assigned to H-3' and H-5'. A quaternary signal at $\delta$ 162.9 was ascribed to C-4' due to its interaction in the HMBC spectrum with the protons at $\delta$ 8.04 (H-2', H-6'). Another quaternary signal at $\delta$ 122.7 was assigned to C-1' due to it is HMBC interactions with the protons at $\delta$ 7.14 (H-3', H-5') and 6.95 (H-3) which in its turn was the confirmation of these protons.

The proton at $\delta$ 6.95 (H-3) appeared as a singlet of one proton [6]. The $^1$H NMR spectrum also showed a pair of doublets showing meta coupling ($J = 2.2$ Hz) at $\delta$ 6.45 and 6.79 each having the integration of one proton and correlated to carbons at $\delta$ 99.7 and 94.8 respectively. These chemical shifts are the characteristic values for C-6 and C-8 in ring A of flavonoids provided C-5, C-7 and C-9 have direct link with oxygen atoms [6, 7].

A signal of three protons integration at $\delta$ 3.86 and its respective carbon at $\delta$ 55.5 showed the presence of methoxyl group in the molecule. This methoxyl group was connected to a quaternary carbon at $\delta$ 162.4 due to the interaction between them in the HMBC spectrum. The quaternary carbon at $\delta$ 162.4 was assigned to C-7 due to its HMBC interaction with H-6 and H-8.

The sugar moiety was connected to C-4' ($\delta$ 162.9) through oxygen due to the interaction between this carbon and anomeric proton of glucose ($\delta$ 5.05). Both sugars were further confirmed by the co-TLC of sugars obtained after the acidic hydrolysis with their authentic samples.

The protons were correlated to their respective carbons with the help of HMQC experiment. The C-C and C-O linkages were confirmed with HMBC and COSY-45° experiments (Fig. 1).

From the spectroscopic evidence and comparative study [5–8] the discussed compound was characterized as 4'-O-rutinosyl genkwanin and named alquds.

**Experimental**

The NMR ($^1$H, $^{13}$C) were recorded on a Bruker AM-400. FABMS (-ve. and +ve.) were recorded on a Jeol-JMS HX-110. The IR and UV spectra were recorded on a Shimadzu IR-46 and a Shimadzu UV-240 respectively.

**Collection, extraction and isolation**

Fresh *Calamintha incana* (2 kg) was collected from the region of Al-Khalil city in Southern of Palestine and identified by Prof. Dawood Al-Asawi from Biology department, University of...
Jordan, Amman. The plant was shade dried and finally, chopped.

The dried plant material was extracted repeatedly with methanol at room temperature. The combined methanolic extracts were evaporated under reduced pressure. The dried extract was separated into six parts (hexane, CHCl₃, 10% MeOH/CHCl₃, 20% MeOH/CHCl₃, 30% MeOH/CHCl₃ and MeOH) by using VLC technique. Alquds was purified by the repeated column chromatography of the fraction obtained with 30% MeOH/CHCl₃.

**Alquds**: m.p. 252–254 °C; UV λmax (MeOH) nm 264.2, 322.6; IR νmax (KBr) cm⁻¹ 3450, 2900, 1850, 1620, 1500; FAB (+ve) 593 [M+H]⁺, m/z 447 [(M+H)-rhm]⁺, 285 [(M+H)-(glc+rhm)]⁺; NMR (¹H, ¹³C) Table.

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