

KAEMPFEROL GLYCOSIDES FROM *Allium cepa* AND *Raphanus sativus*

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We studied flavonoids from *Allium cepa* L. (onion, Liliaceae) and *Raphanus sativus* L. var. *radicula* Pers. (radish, Brassicaceae) in order to isolate biologically active phenolic compounds.

Onion husks remaining after removing the seeds were ground and extracted eight times with CH₃OH. The solvent was evaporated in vacuo. The solid was chromatographed over a silica-gel column with gradient elution by CHCl₃:CH₃OH (95:5-70:30).

Elution of the column by CHCl₃:CH₃OH (90:10) gave **1**.

Compound 1, C₂₁H₂₀O₁₁, mp 209-211°C. The UV spectrum (λ_{\max} 267.5, 297, 351 nm) was consistent with a flavonol derivative. UV spectra recorded with added ionizing and complexing reagents established that free phenolic hydroxyls were present at the 5-, 7-, and 4'-positions of the flavonol core [1]. The IR spectrum contained absorption bands for hydroxyls (3440-3290 cm⁻¹), γ -pyrone carbonyl (1670 cm⁻¹), aromatic double bonds (1618, 1521 cm⁻¹), and glycoside C-O (1100-1000 cm⁻¹).

The PMR spectrum (100 MHz, C₅D₅N, δ , ppm, J/Hz) of **1** exhibited signals for aromatic protons of a 3,5,7,4'-tetrasubstituted flavone core at 6.50 (1H, d, J = 2.0, H-6), 6.55 (1H, d, J = 2.0, H-8), 8.32 (2H, d, J = 9.0, H-2', H-6'), and 7.21 (2H, d, J = 9.0, H-3', H-5'), an anomeric proton at 5.44 (1H, d, J = 7.0, H-1''), and other protons of the carbohydrate at 3.66-4.46 (6H, m).

Acid hydrolysis of **1** gave kaempferol (**2**, C₁₅H₁₀O₆, [M]⁺ 286, mp 269-272°C, λ_{\max} 267, 325 (overlap.), and 368 nm) and D-glucose. A comparison of the UV spectra of **1** and kaempferol showed that the carbohydrate in the former was bonded to the C-3 hydroxyl [1].

Based on the results, **1** was identified as kaempferol-3-O- β -D-glucopyranoside (astragalol) [2].

Compound **1** was isolated from *A. cepa* for the first time.

We investigated the alcohol extract of radish leaves by evaporating it and chromatographing the solid over a column of silica gel.

Elution of the column by CHCl₃:CH₃OH (90:10) gave **3**, C₂₇H₃₀O₁₄, mp 185-186°C. UV spectrum (EtOH, λ_{\max} , nm): 266, 320, 347.

The PMR spectrum (100 MHz, C₅D₅N, δ , ppm, J/Hz) of **3** exhibited signals for aglycon protons at 6.61 (1H, d, J = 2.0, H-6), 6.80 (1H, d, J = 2.0, H-8), 7.94 (2H, d, J = 9.0, H-2', H-6'), and 7.15 (2H, d, J = 9.0, H-3', H-5'), an L-rhamnose, two CH₃ groups at 1.30 (3H, d, J = 6.0, -CH₃) and 1.51 (3H, d, J = 5.5, -CH₃), two anomeric protons at 6.09 (1H, br.s, H-1'') and 6.11 (1H, br.s, H-1'''), and other carbohydrate protons at 3.92-4.62 (8H, m).

The chromatographic mobility of **3** is similar to that of a glycoside. Acid hydrolysis of **3** produced kaempferol (**2**) and L-rhamnose.

Therefore, **3** contains two L-rhamnose monomers. The UV spectra of **3** with added AlCl₃ and NaOCH₃ established that free phenolic hydroxyls were present at the 5- and 4'-positions [1].

Based on the results and the literature, **3** was identified as kaempferol-3,7-di-O- α -L-rhamnopyranoside (lespedin) [3], which possesses hypotensor activity [4].

Flavonoid **3** was isolated for the first time from *R. sativus*.

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