

1-1-2004

Phenylpropanoid Glycosides from *Linum olympicum* (Linaceae)

BELMA KONUKLUGİL

ÖZLEM BAHADIR

Follow this and additional works at: <https://journals.tubitak.gov.tr/chem>

 Part of the [Chemistry Commons](#)

Recommended Citation

KONUKLUGİL, BELMA and BAHADIR, ÖZLEM (2004) "Phenylpropanoid Glycosides from *Linum olympicum* (Linaceae)," *Turkish Journal of Chemistry*. Vol. 28: No. 6, Article 8. Available at: <https://journals.tubitak.gov.tr/chem/vol28/iss6/8>

This Article is brought to you for free and open access by TÜBİTAK Academic Journals. It has been accepted for inclusion in Turkish Journal of Chemistry by an authorized editor of TÜBİTAK Academic Journals. For more information, please contact academic.publications@tubitak.gov.tr.

Phenylpropanoid Glycosides from *Linum olympicum* (Linaceae)

Belma KONUKLUGİL*, Özlem BAHADIR

Department of Pharmacognosy, Faculty of Pharmacy, Ankara University,
06100, Tandoğan, Ankara-TURKEY
e-mail: konuklugil@pharmacy.edu.tr

Received 06.04.2004

The lignan content of *Linum olympicum* Boiss. was investigated by HPLC and GC-MS in comparison with standards, and 2 phenylpropanoid glycosides, syringin (**1**) and coniferin (**2**), were isolated from the aerial parts. Identification of the 2 compounds was achieved by comparison with standards using TLC and HPLC and the structures of the isolated compounds were established by UV and ¹H-NMR analysis.

Key Words: Coniferin, Linaceae, *Linum olympicum*, Phenylpropanoid glycosides, Syringin

Introduction

The genus *Linum* belongs to the family Linaceae and comprises about 200 species mainly distributed in the Mediterranean region. This genus is represented by 39 species in Turkey^{1,2}. To date, lignans, especially aryltetralin group lignans, have been isolated from Turkish *Linum* species. Syringin (**1**) and coniferin (**2**) are phenylpropanoid glycosides and in previous studies coniferin (**2**) was isolated from *L. flavum* and *L. capitatum*³, and syringin (**1**) and coniferin (**2**) were isolated from *L. flavum* var. *compactum*⁴. In this report we describe the isolation and structural identification of the phenylpropanoid glycosides syringin (**1**) and coniferin (**2**) from *L. olympicum* Boiss., which is an endemic species. The lignan content of this species was investigated by HPLC and GC-MS in comparison with standards. This is the first phytochemical study on *L. olympicum*.

Experimental

General Experimental Procedures: NMR measurements in methanol-*d* were recorded on a Bruker DRX 500 spectrometer operating at 500 MHz for ¹H. UV (λ_{max}) spectra were recorded on a Shimadzu UV-160 spectrometer. GC-MS analyses were performed on a Unicam 610 GC-MS (column: WCOT fused-silica CP-Sil 5 CB (15 mm x 0.31 mm i.d., film thickness, 0.25 μ m; Chrompack; Middelburg; the Netherlands)). HP 1100 was used for HPLC analyses (column: C-18-RP 5 μ m, 25 cm x 4.6 mm i.d.). Silica gel 60 GF₂₅₄

*Corresponding author

(Merck) was used for separation on preparative TLC and plates were coated with 0.5 mm thickness silica. TLC analyses were carried out on pre-coated silica gel 60 F₂₅₄ aluminium sheets (Merck). Compounds were detected by UV and by spraying HNO₃: acetic acid (3:10) followed by heating.

Plant Materials: *L. olympicum* was collected from Uludağ, Bursa, 2245 m, in Turkey in September 2002 and identified by Prof. Hayri Duman from the Department of Biology (Gazi University). A voucher specimen (AEF no: 22951) has been deposited in the herbarium of the Department of Pharmaceutical Botany, Faculty of Pharmacy (University of Ankara).

Extraction and Isolation

The dried aerial parts (284.73 g) of *L. olympicum* were powdered and extracted 3 times with MeOH (1.5 L x 3) at 70 °C. The combined MeOH extract was evaporated under reduced pressure to give a crude extract (43.76 g). The crude MeOH extract (11.94 g) was chromatographed by preparative TLC on silica gel layers using CH₂Cl₂:MeOH (85:15) as the solvent system to give a glycoside band. The glycoside band was eluted with Me₂CO:MeOH (1:1) and was then rechromatographed by preparative TLC on silica gel layers with CHCl₃:MeOH (5:1)⁵. Further purification of each compound was carried out by preparative TLC using CHCl₃:MeOH (5:1), EtOAc:MeOH:H₂O (100:16.5:13.5) as solvent systems to yield syringin (**1**) (42 mg) and coniferin (**2**) (35 mg).

GC-MS Analysis

The lignan content of *L. olympicum* was investigated by HPLC and GC-MS. Samples for GC-MS were prepared from air-dried parts of *L. olympicum* as reported in the literature⁶. Polygamain, hinokinin, isojusticidin, morelensin, bursehernin, podophyllotoxin, 6-methoxypodophyllotoxin, β -peltatin and β -peltatin-A-methylether were used as standards. The oven temperature program was 150 to 320 °C at 15 °C/min and 320 °C maintained for 5 min. The injector temperature was 260 °C. The carrier gas used was helium with a split ratio of 20:1. The injected volume was 4 μ L. To obtain mass spectra, electron impact ionization (70eV) was used with an ion source temperature of 250 °C, interface temperature of 280 °C, a scan speed of 2 scans/s and mass range of 34-600 u. The acquired data were stored and afterwards analysed with Lucy Display V2.70 software⁶.

None of these compounds were detected in *L. olympicum*.

HPLC Analysis

Three different samples were prepared from *L. olympicum* as reported in the literature for podophyllotoxin and 6-methoxypodophyllotoxin analyses with HPLC. For elution we used gradient system acetonitrile-water⁷⁻¹⁰.

This study shows that these compounds were not detected in *L. olympicum*.

Results

The known lignans, used as standards for HPLC and GC-MS analysis, were not detected in *L. olympicum*. However, 2 phenylpropanoid glycosides, syringin (**1**) and coniferin (**2**) (Figure), were isolated from this

plant. Identification of the 2 compounds was achieved by comparison with standards on TLC and HPLC and structural elucidation based on $^1\text{H-NMR}$ analysis.

Syringin (**1**): λ_{max} .(MeOH) nm 236, 281; $^1\text{H NMR}$ (500 MHz, methanol-d): Table 1

Coniferin (**2**): λ_{max} .(MeOH) nm 228, 273; $^1\text{H NMR}$ (500 MHz, methanol-d): Table 2

Table 1. $^1\text{H NMR}$ data of syringin.

Proton	δ (ppm) J (Hz)
2, 6 (2H)	6.66 s
1'	6.42 ddd(dt) (1.5, 1.5, 16)
2'	6.25 ddd(dt) (5, 5, 16)
1''	4.66 d (7)
3'(2H)	4.10 br dd
Ome at C-3 and C-5(6H)	3.74 s
6''a	3.65 br dd (2, 11)
6''b	3.53 br dd (6, 11)
2''-5''	3.1-3.4 m.

Table 2. $^1\text{H NMR}$ data of coniferin.

Proton	δ (ppm) J (Hz)
5	7.12 d (8)
2	7.11 d (2)
6	6.93 dd (2, 8)
1'	6.55 ddd(dt) (1.5, 1.5, 16)
2'	6.32 ddd(dt) (5, 5, 16)
1''	4.93 d (7)
3' (2H)	4.22 dd (1.5, 5)
Ome at C-3	3.88 s
6''a	3.875 dd (2, 12)
6''b	3.70 dd (5, 12)
2''-5''	3.3-3.6 m.

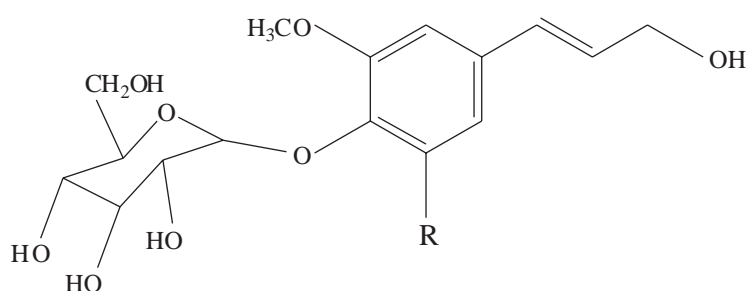


Figure. Phenylpropanoid glycosides from *L. olympicum*.

Discussion

In previous studies on Turkish *Linum* species, lignans, especially aryltetralin group lignans, and phenylpropanoids were isolated. Phytochemical studies are continuing on this genus. This is the first phytochemical study on *L. olympicum*. The known lignan compounds, which were used as standards, were not detected in *L. olympicum* but 2 phenylpropanoid glycosides were isolated. Syringin is the methoxy analogue of

coniferin. Coniferyl alcohol, which is the aglycone of coniferin, is known to be a biosynthetic precursor of lignans³. Two coniferyl alcohol moieties dimerise in early steps in lignan biosynthesis^{11,12}. Further studies on *L. olympicum* will be performed.

Acknowledgements

This study was supported by the University of Ankara (Project No: 2002-08-03-034). The authors thank Prof. Hayri Duman for identifying the plant, Prof. Schimdt for the NMR analysis of the compounds isolated and Dr. Koulman for the GC-MS.

References

1. P.H. Davis, “**Flora of Turkey and The East Aegean Islands**”, Vol. 2., pp. 425-450, University Press, Edinburgh, 1967.
2. A. Güner, N. Özhatay, T. Ekim and K.H.C. Başer, “**Flora of Turkey and the East Aegean Islands**”, Vol. 11., pp. 73, University Press, Edinburgh, 2000.
3. A.J. Broomhead and P.M. Dewick, **Phytochemistry**, **29**, 3839-3844, (1990).
4. B. Konuklugil, **Biochemical Systematics and Ecology**, **25**, 75, (1997).
5. B. Konuklugil, “**A Chemotaxonomic Study of Tumour Inhibitory Aryl Tetralin lignans in *Linum***”, PhD thesis, University of Nottingham, Pharmaceutical Sciences, Nottingham, England, 1993.
6. A. Koulman, R. Bos, M. Medarde, N. Pras and W.J. Quax, **Planta Med.**, **67**, 858- 862, (2001).
7. C. Canel, F.E. Dayan, M. Canzera, I.A. Khan, A. Rimando, C.L. Burandtjr and R.M. Moraes, **Planta Med.**, **67**, 97-99, (2001).
8. U. Empt, W.A. Alfermann, N. Pras and M. Petersen, **Journal of Applied Botany**, **74**, 145-150, (2000).
9. M. Kartal, B. Konuklugil, W.A. Alfermann and G. Indryanto, **Journal of Pharmaceutical and Biomedical Analysis**, **35**, 441-447, (2004).
10. Ö. Bahadır, “**Researching on Component of Aryltetralin and Other Lignan Groups on *Linum olympicum* Boiss.**” Thesis in Pharmacognosy, Faculty of Pharmacy, Ankara University, Ankara, Turkey, 2003.
11. G.A. Molog, U. Empt, S. Kuhlmann, W. Van Uden, N. Pras, A.W. Alfermann and M. Petersen, **Planta**, **214**, 288-294, (2001).
12. V. Seidel, J. Windhovel, G. Eaton, A.W. Alfermann, R.R.J. Arroo, M. Medarde, M. Petersen and J.G. Woolley, **Planta**, **215**, 1031-1039, (2002).