Chemistry of Natural Compounds, Vol. 44, No. 2, 2008

LAVANDOSIDE FROM *Lavandula spica* FLOWERS

V. A. Kurkin,[1] M. Lamrini,[1] and S. G. Klochkov[2]

UDC 615.32:547.97

*The new natural compound lavandoside with the structure ferulic acid 4-*O-β-*D-glucopyranoside was isolated by column chromatography over silica gel and polyamide from the extract of* Lavandula spica *flowers. The chemical structure of lavandoside was established using UV, NMR, and mass spectra and chemical transformations.*

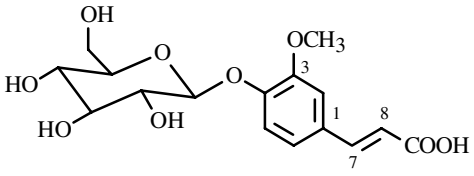
Key words: phenylpropanoids, cinnamic acids, ferulic acid glucoside, lavandoside, *Lavandula spica* L.

Flowers of *Lavandula spica* L. (Lamiaceae) are used in the Russian Federation to produce the bactericidal preparations Livian and Lavandic Alcohol based on essential oil obtained from fresh lavender flowers [1, 2]. This plant is widely used abroad as sedative agents [2-5], among which Nervoflux is registered in the RF. Objective prerequisites on the raw material for fabricating preparations based on lavender flowers have been issued because this Mediterranean plant is widely cultivated in many countries of the world including the RF, republics of the former USSR, and Morocco.

We isolated previously the flavonoids cosmosiin and cinaroside from the extract of lavender flowers [6]. Furthermore, the presence in lavender flowers of luteolin (5,7,3′,4′-tetrahydroxyflavone) has been reported in the foreign literature [7].

The goal of our work was to study in detail the chemical structure of lavender flowers growing in Morocco.

A new natural compound (**1**) that we called lavandoside was isolated from the extract of lavender flowers by column chromatography over silica gel and polyamide.



1

The chemical structure of **1** was established using PMR, UV and mass spectroscopy and chemical transformations.

Compound **1** was cleaved by β-glucosidase (Fluka, Hungary) into glucose and the aglycon, which was identified by comparison with an authentic sample as ferulic acid (**2**) using certain physicochemical and spectral properies and TLC.

The PMR spectrum contained two 1H doublets with spin—spin coupling constant (J) 16.05 Hz at 8.04 and 6.43 ppm that were assigned to protons H-7 and H-8, respectively. This was consistent with the presence of trans-cinnamic acid (a phenylpropanoid) in the molecule. The aromatic ring of **1** had typical 3,4-substitution because the PMR spectrum exhibited characteristic resonances of aromatic protons at 7.60 (1H, d, J = 8.61, H-5), 6.88 (1H, J = 2.33, H-2), and 6.67 (1H, dd, J = 2.33 and 8.61, H-6). The presence of an aromatic methoxyl was confirmed by a 3H singlet at 3.86 ppm.

Resonances of the carbohydrate moiety (glucose) were found in the PMR spectrum as a multiplet (6H) and doublet for the anomeric proton at 5.00 and 4.98 ppm with J = 7.21, typical of H-1′ of β-D-glucopyranose.

Glucose was assigned to the 4-OH group based on the chemical shift of the resonance for the anomeric proton at 5.00 ppm that was observed for glycosylation of the phenolic group. Glycosylation of the carboxylic acid, i.e., formation of an acylglycoside bond, would cause a shift of the resonance for the anomeric proton to weaker field, to about 6.0 ppm [8].

1) GOU VPO Samara State Medical University of Roszdrav, Russia, 443099, ul. Chapaevskaya, 89, fax 7(846) 333 29 76, e-mail: vakur@samaramail.ru; 2) Institute of Physiologically Active Substances, Russian Academy of Sciences, Russia, 142432, Moscow Oblast, Chernogolovka, fax 7(495) 913 21 13, e-mail: klk@ipac.ac.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 133-134, March-April, 2008. Original article submitted January 16, 2008.

0009-3130/08/4402-0169

A compound with a structure similar to that of **1** was isolated from suspension culture of *Chenopodium rubrum*. However, the glucose in this phenylpropanoid was bonded to the carboxyl [9].

Thus, lavandoside (**1**) that was isolated from *L. spica* flowers was a new natural compound with the structure 4-hydroxy-3-methoxycinnamic acid 4-*O*-β-D-glucopyranoside.

EXPERIMENTAL

Flowers of *Lavandula spica* collected in Morocco in a valley of the Atlas Mountains (2006) and dried in air in the shade were used as starting material for the investigation.

Lavender flowers (200 g) were extracted exhaustively with ethanol (70%) by combining grinding (24 h) with subsequent thermal extraction at 85-90°C. The aqueous alcohol extracts were evaporated in vacuo to a thick residue (about 50 mL). The condensed extract was dried over silica gel (L 40/100) to produce a powder (extract + silica gel) that was placed on a layer of silica gel that was pretreated with $CHCl_3$. The chromatography column was eluted with $CHCl_3$ and $CHCl_3$:C_2H_5OH in various ratios (97:3, 95:5, 93:7, 90:10, 88:12, 85:15, 80:20, 70:30). The separation was monitored by TLC.

Fractions containing **1** were combined and placed on Woelm polyamide for further purification. The dry powder (extract + polyamide) was transferred to a chromatography column (sorbent height 4.0 cm, diameter 5 cm) that was eluted with water and aqueous ethanol (20, 40, 70, 96%). The purification over polyamide columns produced **1** (water eluent) that was purified additionally by rechromatography over Sephadex LH-20 with elution by $CHCl_3$ and $CHCl_3$:C_2H_5OH in various ratios (95:5, 93:7, 90:10, 88:12, 85:15, 80:20, 70:30).

UV spectra of **1** and its aglycon (**2**) were recorded on a Specord 40 spectrophotometer (Analytik, Jena). PMR spectra of **1** were recorded on a Bruker 250 spectrometer. Mass spectra were obtained in a Finnigan LXQ LC—MS/MS. Enzymatic hydrolysis of **1** was carried out using β-glucosidase (Fluka, Hungary) at 38°C for 12 h.

Compound 1, amorphous light-yellow compound, $C_{21}H_{20}O_{10}$, mass spectrum (*m/z*, %): 195.01 (24.71) [M (aglycon) + H]$^+$, 176.98 (100.00) [M (aglycon) - H_2O + H]$^+$, 152.97 (28.60) [M (algycon) - COO + H]$^+$. UV spectrum (EtOH, λ_{max}, nm): 281, 313. PMR spectrum (250 MHz, CD_3OD, δ, ppm, J/Hz): 3.3-4.0 (6H, glucose), 3.86 (3H, s, OCH_3), 5.00 (1H, d, J = 7.0, glucopyranose H-1′), 6.44 (1H, d, J = 16.05, H-8), 6.67 (1H, dd, J = 2.33, 8.61, H-6), 6.88 (1H, J = 2.33, H-2), 7.60 (1H, d, J = 8.61, H-5), 8.08 (1H, d, J = 16.05, H-7).

PMR spectrum (250 MHz, CH_3CN:C_6D_6, δ, ppm, J/Hz): 3.20-3.60 (4H, glucose), 3.64 (1H, dd, J = 5, 12, H-6′), 3.76 (3H, s, OCH_3), 3.84 (1H, dd, J = 1.86, 12.10, H-6′), 4.98 (1H, d, J = 7.21, glucopyranose H-1′), 6.43 (1H, d, J = 16.05, H-8), 6.57 (1H, dd, J = 2.33, 8.61, H-6), 6.80 (1H, J = 2.33, H-2), 7.52 (1H, d, J = 8.61, H-5), 8.04 (1H, d, J = 16.05, H-7).

Compound 2, light-yellow crystals, $C_{10}H_{10}O_4$, mp 167-170°C (aqueous alcohol). UV spectrum (EtOH, λ_{max}, nm): 240, 290sh, 318.

REFERENCES

1. V. A. Kurkin, *Pharmacognosy: Textbook for Students of Pharmacy Schools* [in Russian], 2nd Ed., Revised and Supplemented, OOO Ofort, GOU VPO SamGMU, Samara (2007).
2. *State Registry of Drugs* [in Russian], Vol. 1, Official Ed., Meditsina, Moscow (2004).
3. A. Sejilmassi, *Medical Plants in Morocco*, Casablanca (1995), 145.
4. A. T. Nafysi, *Review of Traditional Medicine in Iran*, Isfahan University Publications, Isfahan (1989), 122.
5. H. Wagner, *Pharmazeutische Biologie, Drogen und ihre Inhaltsstoffe*, Gustav Fischer Verlag, Stuttgart-New York (1993).
6. V. A. Kurkin and M. Lamrini, *Khim. Prir. Soedin.*, 582 (2007).
7. J. B. Harborne, *Comparative Biochemistry of the Flavonoids—Phytochemical Unit, The Hartley Botanical Laboratories*, The University of Liverpool, England (1967), 217.
8. V. A. Kurkin, G. G. Zapesochnaya, A. G. Dubichev, E. D. Vorontsov, I. V. Aleksandrova, and R. V. Panova, *Khim. Prir. Soedin.*, 481 (1991).
9. D. Strack and M. Bokern, *Z. Naturforsch. C: J. Biosci.*, **39**, No. 9/10, 902 (1984).