FLAVONOL 3-GLUCOSIDES OF THE OLEORESIN OF Larix sibirica

S. A. Medvedeva, N. A. Tyukavkina,
and S. Z. Ivanova

UDC 547.972

From a methanolic extract of the oleoresin of Larix sibirica Ledb. (Siberian larch), in addition to the flavonoid compounds described previously [1-3], we have isolated three flavonol glycosides by chromatography on polyamide. Substance (I) has the form of greenish-yellow needles with mp 164-166°C (aqueous methanol), $[\alpha]_D^{22}$ −51.83° (c 2.806; pyridine); (II) forms small light-yellow needles with mp 224-226°C (aqueous methanol), $[\alpha]_D^{20}$ −45.75° (c 2.782; pyridine); and (III) is a dark-yellow powder with mp 258-262°C, $[\alpha]_D^{20}$ −36.86° (c 2.71; pyridine).

The PMR spectra of the silyl ethers of the glycosides show similar doublets at δ 5.96-6.1 ppm (1H) and 6.4 ppm (1H), J = 2 Hz, due to H-6 and H-8 of ring A, respectively. The glycosides isolated differ in the structure of ring B. In the PMR spectrum of compound (III) the signal of the protons of ring B forms one singlet at δ 7.17 ppm (2H), corresponding to H-2' and H-6'. In compounds (I) and (II), in addition, there are doublets at δ 6.81 ppm (1H), J = 8 Hz, due to H-5'. However, in the PMR spectrum of compound (I) the signals of the H-6' proton [doublet at δ 7.33 ppm (1H), J = 8 Hz] and of the H-2' proton [singlet at δ 7.71 1H)] are well-separated, while in compound (II) the signals of these protons are superposed, forming an unsymmetrical doublet at δ 7.47 ppm (2H). In addition, compound (I) has a singlet at δ 3.83 ppm (3H), assigned to a methoxy group. The 3' position of the methoxy group was determined by the alkaline decomposition of the aglycone of compounds (I), which gave vanillic acid.

The PMR spectra of the glycosides studied each had a doublet at δ 5.83 ppm, J = 7 Hz, related to the anomeric proton of a glycoside substituent in position 3 attached by a β-glycosidic linkage [4, 5]. This signal and a multiplet in the δ 3.25-3.75-ppm region (6H), corresponding to the other protons of the carbohydrate substituent, were absent from the spectra of the corresponding aglycones.

The position of the carbohydrate substituent was confirmed by UV spectroscopy. The strong bathochromic shift of the first band for the aglycones on the addition of $AlCl_3$, as compared with the glycosides, with the simultaneous increase in the intensity of this band is in harmony with position 3 of the carbohydrate substituent. The pyranose form of the ring was determined by a molecular-rotation calculation [6].

The acid hydrolysis of the glycosides gave the corresponding aglycones and D-glucose in a ratio of 1 : 1. The glucose was identified by the GLC method in the form of the silyl ether [7] on a Tswett-2 instrument with a flame-ionization detector using nitrogen as the carrier gas and 10% of E-301 on Chromosorb W (45-60 mm) as the stationary phase and a temperature of 175°C and in the form of the aldononitrile acetate [8] on the same instrument using 15% butanediol succinate on Chromosorb W treated with acid and dichlorodimethylsilane as stationary phase, at temperatures of 100-225°C. The analysis was performed in the carbohydrate laboratory of the Far-Eastern Scientific Center, Academy of Sciences of the USSR by I. N. Krasikova.

From their physicochemical constants and a chromatographic comparison with authentic samples, the aglycones were identified as isorhamnetin, quercetin, and myricetin.

Irkut-sk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 800-801, November-December, 1972. Original article submitted May 22, 1972.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $15.00.

Thus, the glycosides isolated from the oleoresin of the Siberian larch were isorhamnetin 3-β-D-glucopyranoside, quercetin 3-β-D-glucopyranoside, and myricetin 3-β-D-glucopyranoside. The isolation of the two latter glycosides from the oleoresin of the genus Larix has not been reported in the literature.

The PMR spectra of the silyl ethers of the glycosides and of the aglycones [9] were taken on a BS487B instrument in CCl_4 with hexamethyldisiloxane as internal standard. The samples of isorhamnetin, myricetin, and quercetin 3-glucosides were kindly given to us by L. I. Dranik.

LITERATURE CITED

1. S. A. Medvedeva, N. A. Tyukavkina, and S. Z. Ivanova, Khim. Prirodn. Soedin., 123 (1972).
2. N. A. Tyukavkina, S. A. Medvedeva, S. Z. Ivanova, and V. K. Voronov, Khim. Prirodn. Soedin., 674 (1972).
3. S. A. Medvedeva and N. A. Tyukavkina, Khim. Prirodn. Soedin., 676 (1972).
4. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Berlin, Springer-Verlag (1970), p. 268.
5. R. U. Lemieux and J. D. Stevens, Can. J. Chem., 43, 2059 (1965).
6. I. P. Kovalev and V. I. Litvinenko, Khim. Prirodn. Soedin., 233 (1965).
7. J. Kagan and T. J. Mabry, Anal. Chem., 37, 288 (1965).
8. V. M. Easterwood and B. J. L. Huff, Svensk Papperstidn., 72, 768 (1969).
9. T. J. Mabry, J. Kagan, and H. Rosler, Phytochem., 4, 177 (1965).