Tetrahedron Letters No. 11, pp. 803-804, 1970. Pergamon Press. Printed in Great Britain.

ISOLATION AND STRUCTURE OF THE 3-GALACTOSIDE OF A NEW FLAVONOL 5,7,3',4'-TETRAHYDROXY-8-METHOXY-FLAVONOL (CORNICULATUSIN) FROM LOTUS CORNICULATUS L. (1)

Jørn Gry Nielsen

Chemical Laboratory B, The Royal Danish School of Pharmacy, Copenhagen, Denmark

(Received in UK December 22 1969; accepted for publication January 29 1970)

So far the isolation and structural elucidation of three flavonoid glycosides from the genus Lotus L. (Leguminosae) have been recorded (2,3). This communication will discuss the structure determination of a new flavonol glycoside, which was isolated from the flowers of Lotus corniculatus L. by column chromatography on polyamide and cellulose. Mp 216-217°; λ_{max}^{MeOH} 262, 273, and 366 nm. The structure 5,7,3',4'-tetrahydroxy-8-methoxy-flavonol-3-O-β-D-galactoside (I) of the flavonoid was based on the following data:

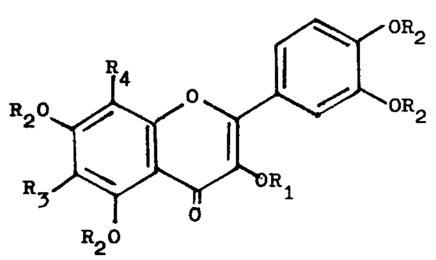
The nmr spectrum (60 MHz) of the per-trimethylsilylated glycoside in CCl_4 (5) showed a pattern typical of a flavonoid having 3',4'-oxygenation in ring B. One other flavone nucleus proton gave a singlet at δ 6.18, which could be attributed to H-3, H-6 or H-8. The spectrum also showed a methoxyl group at δ 3.86 (s, 3H), hexose H-1 at δ 5.67 (d, 1H) and multiplets between δ 3.3 and δ 4.0 (6H).

Upon adding the usual diagnostic reagents the uv spectra of (I) suggested the presence of free hydroxyls at C-5, C-7, C-3', and C-4', and the absence of a free hydroxyl at C-3 (5).

By hydrolyzing (I) with β-D-galactosidase (6) and by comparing the released carbohydrate with authentic material (tlc), the sugar residue was shown to be β-linked D-galactose.

For the aglycone (II), mp 275-277°, which is termed corniculatusin, the existence of a free 3-OH was established by the characteristic behaviour in uv of band I, after adding $AlCl_3$/HCl or NaOMe (5).

The nmr spectrum of the fully trimethylsilylated aglycone was in accordance with a 3,5,7,8,3',4'- or 3,5,6,7,3',4'-hexasubstituted, monomethylated flavone. After selective detrimethylsilylation at C-5, the appearance of a signal at δ 11.90, combined with a shift of less than 0.05 ppm for the A-ring signal, indi-



I R_1=β-D-galactosyl, R_2=R_3=H, R_4=methoxy
II R_1=R_2=R_3=H, R_4=methoxy
III R_1=R_3=H, R_2=methyl, R_4=methoxy
IV R_1=R_2=methyl, R_3=H, R_4=methoxy
V R_1=R_2=R_4=H, R_3=methoxy
VI R_1=R_2=methyl, R_3=methoxy, R_4=H

cated the presence of a free 5-OH and an aromatic proton at C-6 (5).

Permethylation of (I), followed by hydrolysis, furnished a compound, mp 234-235°, which was shown to have the structure 3-hydroxy-5,7,8,3′-4′-pentamethoxy-flavone (III) by nmr, uv (64 nm bathochromic shift of band I in $AlCl_3$/HCl), and mass spectral data (M^+ m/e 388, $C_{20}H_{20}O_8$). Methylation of (III) yielded 3,5,7,8,3′,4′-hexamethoxy-flavone (IV) (M^+ m/e 402, $C_{21}H_{22}O_8$), mp 159-160° and 170-171° (dimorphism) (ref. 7, mp 159-161° and 170-171°).

The structure (I) was further supported by the mass spectrum of the aglycone (II) which rendered abundant peaks at m/e 332 (M^+), 317 (demethylation at 8-OCH_3), 303 (M^+-CHO, involving 3-OH), 167 and 139 (A-ring fragments with 5 and 4 oxygens), 137 and 109 (B-ring fragments with 3 and 2 oxygens) (8).

At this stage the 3-O-β-D-galactoside of the 6-methoxy isomer, patuletin (V) was excluded on following grounds: The chemical shift of the A-ring proton after specific detrimethylsilylation and the deviation in the melting points of (V), 261-263° and (VI), 143-144° (9) from (II) and (IV), respectively.

An unequivocal proof of the structure (I) was obtained by synthesizing (II), corniculatusin, and (V) patuletin (4).

Acknowledgements. The author wishes to thank Prof. H.Kofod for laboratory facilities and Statens Naturvidenskabelige Forskningsråd, Copenhagen, for financial aid.

References

1. Flavonoids of Lotus L.I; for part II see ref..4.
2. T. Nakaoki, N.Morita, A.Hiraki, and Y. Kurokawa, J.Pharm.Soc.Japan 76,347(1956).
3. J.B.Harborne, Phytochemistry 8,177(1969).
4. J.G.Nielsen, P.Nørgaard, and H.Hjeds, unpublished results.
5. T.J.Mabry in Perspectives in Phytochemistry, Academic Press, New York, 1969.
6. F.Engbeck is thanked for a gift of β-D-galactosidase.
7. C.A.Henrick and P.R.Jeffries, Aust.J.Chem. 17,934(1964).
8. J.H.Bowie and D.W.Cameron, Aust.J.Chem. 19,1627(1966).
9. A.Zane and S.H.Wender, J.Org.Chem. 26,4718(1961).