

FLAVONOL GLYCOSIDES OF *ANTHYLLIS VULNERARIA* LEAVES

JEAN-FRANÇOIS GONNET

Service de Phytochimie, Département de Biologie Végétale, Université Claude-Bernard Lyon I,
43, boulevard du 11 Novembre 1918 F - 69621 Villeurbanne, France

(Received 10 October 1974)

Key Word Index—*Anthyllis vulneraria*; Leguminosae; flavonols: quercetin, kaempferol and isorhamnetin glycosides; 3-*O*-arabinosides.

Plant material. Leaves of *A. vulneraria* from experimental populations cultivated in Botanical Garden, Science Faculty of F-91405 ORSAY (where herbarium specimen are deposited). **Previous work.** Leaves: quercetin, kaempferol, isorhamnetin [1, 2], rhamnetin, rhamnocitrin, desoxy-5 flavonols [3]; quercetin 3-*O*-arabinoside-7-*O*-glucoside [4].

Present work. Intraspecific chemical investigation of 27 populations of *A. vulneraria* showed the presence of about 35 flavonol glycosides [5]. Major constituents have been identified as: quercetin 3-*O*-glucoside (A), 3-*O*-galactoside (B) and 3-*O*-arabinoside (polystacchoside, C), kaempferol 3-*O*-galactoside (D) and 3-*O*-arabinoside (E), isorhamnetin 3-*O*-galactoside (F) and 3-*O*-arabinoside (G). Other compounds are presently under investigation.

EXPERIMENTAL

Dried leaves (200 g) were extracted (3 × 24 hr) with MeOH-H₂O: 6:4 (31); after filtration and concentration, the extract was taken up with H₂O. Monosides (essentially) were then extracted with EtOAc; column chromatography of part of the EtOAc extract on polyamide (elution with C₆H₆-MeOH: 1:1)

yielded pure amounts of B (20 mg), C (2 mg) and F (20 mg). Preparative twodimensional TLC on polyamide (1: C₆H₆-MeCOEt-MeOH: 25: 10: 11, 2: H₂O-MeOH-MeCOEt-acetylacetone: 30: 15: 10: 4) provided small amounts of A, D, E and G. All were monosides (*R_f* 0.15 on polyamide TLC with Egger's solvent [6]) with 3-OH links (dark purple under UV light and set of 6 UV spectra [7]).

After acid hydrolysis (HCl 2 N, 40 mn, 100°), aglycones were removed (EtOAc) from hydrolysate and identified by co-chromatography (TLC) on polyamide (C₆H₆-MeCOEt-MeOH: 6:1:3) with authentic markers of quercetin, kaempferol and isorhamnetin.

Sugar identification, after reduction and acetylation [8], was carried out by GLC using a 2 m × 2 mm glass column packed with 100-120 mesh 3% ECNSS on Gas Chrom Q. IR spectra of B and F were identical with IR spectra of authentic samples.

REFERENCES

1. Kowaleski, Z. and Kowalska, M. (1966) *Chem. Abst.* **65**, 15787 f.
2. Letoublon, R. (1968) *Diplôme d'Etudes Supérieures*, Lyon.
3. Gonnet, J. F. and Jay, M. (1972) *Phytochemistry* **11**, 2313.
4. Gonnet, J. F. (1972) *C. R. Acad. Sci. Paris* **275**, 117.
5. Gonnet, J. F. (1974) *Thèse Doctorat Spécialité*, Lyon.
6. Egger, K. (1961) *Z. Anal. Chem.* **182**, 161.
7. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) in *The Systematic Identification of Flavonoids*, Springer, Heidelberg.
8. Oades, J. M. (1967) *J. Chrom.* **28**, 246.