Phytochemistry, Vol. 20, No. 6, pp. 1421–1422, 1981.
Printed in Great Britain.

0031-9422/81/061421-02 $02.00/0

IRIDOID GLUCOSIDES OF *ODONTITES VERNA*

ARMANDODORIANO BIANCO*‡, ANNA FRANCESCONI† and PIETRO PASSACANTILLI*

*Centro CNR per lo Studio della Chimica delle Sostanze Organiche Naturali, Istituto di Chimica Organica della Università, P. le Aldo Moro n.5 00185, Roma, Italy; †Istituto di Botanica dell'Università di Roma, Roma, Italy

(*Revised received* 31 *March* 1980)

Key Word Index—*Odontites verna* subsp. *serotina*; Scrophulariaceae; iridoid glucosides; mussaenoside; shanzhiside methyl ester; aucubin; odontoside; catalpol.

Abstract—Five iridoids have been identified in the whole plant of *Odontites verna*.

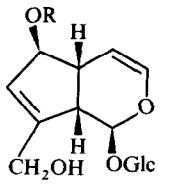
We have examined the presence of iridoid glucosides in dicotyledons in relation to the habitat in which these plants grow and the native flora in the neighbourhood of Rome, and tested samples of *Odontites verna* subsp. *serotina* Dumort [1]. This herbaceous plant is common in meadows and uncultivated lands in Italy and may often be semiparasitic. It blooms between the spring and autumn depending on the weather. The plant is generally 20–50 cm high with ascendent and outwardly erect branches, the corollas are red-violet and the leaves are slightly narrow at the base and pubescent.

O. *verna* subsp. *serotina* was collected in October at the Villa Doria-Pamphili (Rome) when it was in flower. A voucher specimen of this plant was identified in the Herbarium of Istituto di Botanica dell'Università di Roma. Ethanolic extracts of the whole plant, worked up using the charcoal method [2], gave two iridoid fractions: the first was obtained by elution with 30% EtOH (fraction A) and the second with 50% and 80% EtOH (fraction B). From fraction B five products were isolated by chromatography on cellulose (Whatman CF11) in *n*-BuOH saturated with H_2O (BW). Each iridoid was successively purified by chromatography on silica gel in $CHCl_3$–MeOH (4:1). Two of those found were aucubin (**1**) (0.06% yield) and odontoside (**2**) (0.06% yield) whose presence in this plant has been previously described [3, 4]. Two other iridoids proved to be identical with mussaenoside (**3**:0.008% yield) and shanzhiside methyl ester (**4**:0.02% yield). These compounds have previously been isolated from rubiaceous plants (*Mussaenda parviflora* and *M. shikokiana*) by Takeda *et al.* [5] and never previously found in the Scrophulariaceae. It should be noted that *Veronica* (Scrophulariaceae) contains an iridoid (ladrol [6]) whose structure is similar to **3**; the stereochemistry of the C-8 centre has unfortunately not yet been determined.

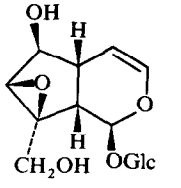
Compound **3** was readily identified by physical data ($[\alpha]_D$, ^{1}H NMR) and those of its tetraacetate (mp, $[\alpha]_D$, ^{1}H NMR) which were exactly the same as those reported [5].

It is interesting that compound **4** was obtained for the first time in crystalline form (Me_2CO–EtOAc, 4:1), mp 118.5–119.5° (uncorr.); its $[\alpha]_D^{30}$ −127.0° (MeOH; *c* 0.45) differed from that reported (lit. [5] $[\alpha]_D^{30}$ −110.8° (MeOH; *c* 0.42)); ^{1}H NMR (90 MHz, D_2O): δ 7.48 (1H, *d*, $J_{3,5}$ = 1.0 Hz, C-3), 5.62 (1H, *d*, $J_{1,9}$ = 2.0 Hz, C-1), 4.15 (1H, *dt*, $J_{6,7\alpha} = J_{6,7\beta}$ = 6.5, $J_{6,5}$ = 3.0 Hz, C-6), 3.79 (3H, CO_2Me), 3.03 (1H, *b. dd*, $J_{5,6}$ = 3.0, $J_{5,9}$ = 10.0 Hz, C-5), 2.71 (1H, *dd*, $J_{9,1}$ = 2.0, $J_{9,5}$ = 10.0 Hz, C-9), 2.00 (2H, 8 lines, $J_{7\alpha,7\beta}$ = 13.5, $J_{7\alpha,6} = J_{7\beta,6}$ = 6.5 Hz, C-7), 1.29 (3H, *s*, Me). Compound **4** afforded a crystalline pentaacetate (EtOH), mp 189.5–190.5°; $[\alpha]_D^{30}$ −105.5° ($CHCl_3$; *c* 0.5) (lit. [4] mp 173–175°; $[\alpha]_D^{30}$ −111.9° ($CHCl_3$; *c* 0.67)); ^{1}H NMR (90 MHz, $CDCl_3$), however, is exactly superimposable with that reported in ref. [4].

The fifth iridoid is a glucoside with a molecular formula $C_{17}H_{26}O_{10}$ like that of **3**. Its ^{1}H NMR spectrum (90 MHz, D_2O) showed a broad singlet at δ 7.45 attributable to the olefinic H-3 proton, a singlet at 3.75 due to a carbomethoxy group and a doublet at 1.05 (J = 7.0 Hz) attributable to a methyl group geminal with a proton. Research is in progress on the structure and configuration of this iridoid.



1 R = H
2 R = *p*-coumaroyl



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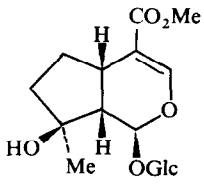

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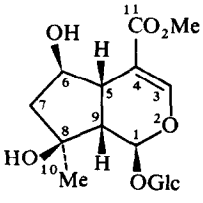

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‡To whom communications should be addressed.

From fraction A we isolated five further iridoid products by chromatography on cellulose in BW: the more abundant (0.06% yield) was identical to catalpol (**5**) recently found in this plant [3,4]; the other four iridoids are at the moment unidentified.

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