Finally, the acetyl groups was located on the glucosyl C-2 hydroxy group by a double resonance experiment irradiation of the glucosyl H-1 converted the double doublet at δ 5 68 into a simple doublet

EXPERIMENTAL

The plant material was provided by Mr M F De Carvalho, Scientific Investigation Institute, Agronomic Section, Lourenço Marques (Mozambique) A herbarium specimen is available at the Department of Pharmacognosy, Inverni della Beffa, Milan, Italy

M ps were corrected NMR were recorded on a Varian XL-100 instrument MS were obtained on a Varian CH7 spectrometer and IR on a Perkin-Elmer model 157G instrument UV was measured on a DBGT Beckmann spectrophotometer

Isolation of flavonoids from B zanguebarica The dry leaves were extracted at 30° with 90% aq MeOH After concentration, extraction with $CHCl_3$ and column chromatography [eluent AcOEt–EtOH–H_2O (100 13 5 10), silica gel] afforded *sequojaflavone* and *vitexin 2″-O-acetyl 7-O-methyl ether* (**1**) Extraction with *n*-BuOH yielded, after column chromatography [silica gel, eluent $CHCl_3$–MeOH–H_2O (13 7 2), lower phase], *vitexin* and *isoorientin*

Vitexin 2″-O-acetyl 7-O-methyl ether The flavonoid (**1**) showed the following properties m p 180° (AcOEt), $[\alpha]_D$ −63° (*c* 0 5, pyr), λ_{max} (MeOH) 266, 298 sh, 333 nm λ_{max} (MeONa) 253, 268, 298 sh, 388 nm, λ_{max} ($AlCl_3$) 274, 302, 340, 387 nm, λ_{max} ($AlCl_3$–HCl) 274, 300, 337, 383 nm, λ_{max} (AcONa) 258 sh, 268, 299 sh, 391 nm, λ_{max} (AcONa–H_3BO_3) 267, 298 sh, 337 nm, MS *m/e* 488 (M^+), 469, 445, 428, 427, 413, 396, 326, 313, 297, 255, 179, 118, 121, IR (KBr) 3400 1745 1655 cm^{-1}

Vitexin 7-O-methyl ether The HCl-hydrolyzed product from (**1**) showed the following properties m p 200° (H_2O), M^+ = 466, NMR signals after silylation (CCl_4, δ) 7 87 (*d*, *J* 10 Hz, H-2′ and H-6′) 6 84 (*d*, *J* 10 Hz, H-3′ and H-5′), 6 34 (*s*, H-3), 6 24 (*s*, H-6), 4 89 (*d*, *J* 10 Hz, H-1″), 3 83 (*s*, MeO–) and six protons between 4 4 and 3 1, IR (KBr) 3400, 1655 cm^{-1}

Oxidation of (**1**) *with* $FeCl_3$ was carried out in aq soln by heating in an oil-bath at 125 for 6 hr Filtration through a column of silica gel using water as eluent and concentration yielded a syrup which on PC showed identity with glucose

Acetylation of both (**1**) and the HCl-hydrolyzed product (**3**) m p 177 (*iso*-Pr_2O) NMR acetate signals ($CDCl_3$, δ) at 2 40 (C-5), 2 30 (C-4) 2 05 (C-4′) 1 95 (C-3″), 1 87 (C-6′), 1 70 (C-2′)

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FUROCHROMONES OF *ERANTHIS PINNATIFIDA*

HIROSHI WADA, MITSUNORI GAINO and SEIICHI SAITO

Organic Chemistry Research Laboratory Tanabe Seiyaku Co Ltd Kawagishi 2-2-50 Toda Saitama Japan

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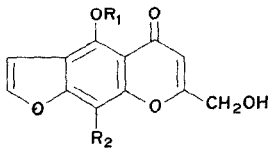
Key Word Index—*Eranthis pinnatifida*, Ranunculaceae, khellol, norkhellol cimifugin new furochromones

In earlier work on the chromone constituents of *Eranthis*, khellol glucoside was only found in *E hyemalis*[1] In this communication we wish to report five chromones from *E pinnatifida* Maxim all of which have 7-hydroxymethyl groups

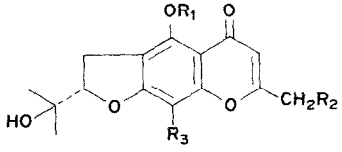
The MeOH extract of the leaves and stems collected at the flowering season afforded, after chromatographic separation, five chromones, khellol (**1**),[2] norkhellol (**2**)[3] and three

[1] EGGER, K (1961) *Z Naturforsch* **16b**, 697
[2] SPATH, E and GRUBER, W (1941) *Chem Ber* **74**, 1549
[3] SCHONBERG, A and AZIZ, G (1953) *J Am Chem Soc* **75**, 3265

new chromones, cimifugin (**3**) m p 128–130°, norcimifugin (**4**) m p 191° and norammiol (**5**) m p 242°



(**1**) R_1 = Me, R_2 = H
(**2**) R_1 = H, R_2 = H
(**5**) R_1 = H, R_2 = OMe



(**3**) R_1 = Me, R_2 = OH, R_3 = H
(**4**) R_1 = H, R_2 = OH, R_3 = H
(**7**) R_1 = OMe, R_2 = Cl, R_3 = H
(**8**) R_1 = H, R_2 = H, R_3 = H
(**9**) R_1 = H, R_2 = H, R_3 = I

The first crystalline compound (**3**) $C_{16}H_{18}O_6$, m p 128–130° on recrystallization from C_6H_6–Me_2CO, whose hydrated sample m p 107° was also prepared from aq MeOH, showed $[\alpha]_D$ + 78°, characteristic UV[λ_{max}^{MeOH} 229, 250 (inf), 293 nm] and IR (ν_{max}^{KBr} 3380, 1660, 1610 cm^{-1}) The NMR spectrum[4] indicated the presence of two tertiary methyl groups (1 36, 6H, *s*), a methylene group (3 45, 2H, *d*, *J* 9), a methoxyl group (4 06 3H *s*), a hydroxymethyl group (a methylene group 4 55, 2H, *d*, *J* 6 2, a hydroxyl group 5 91, 1H, *t*, *J* 6 2), a tertiary hydroxyl group (4 93, 1H, s), a methine proton (4 95 1H, *t*, *J* 9) and two aromatic protons (6 3, 1H, *s*, 6 83, 1H, s) The structure of **3**, which was deduced from the spectroscopic data, was further established by transformation to visamminol (**6**) The treatment of **3** with mesyl chloride in pyridine afforded a chloride (**7**) which was reduced and demethylated with NaI in refluxing AcOH to give a deoxy compound (**8**) $C_{15}H_{16}O_5$, accompanied with an iodide (**9**)[5] $C_{15}H_{15}IO_5$, m p 147° The deoxy compound **8** was identical with visamminol (**6**)[6] by m m p and IR, MS spectral comparisons Therefore the structure of **3** was concluded to be 2,3-dihydro-2-isopropyloxy-4-methoxy-7-hydroxymethyl-furochromone When our work was in progress the structure of **3** was given by Takemoto for cimifugin[7] m p 107° which was isolated from *Cimicifuga simplex* Wormsk The hydrated sample of **3**, m p 107° was found to be identical with an authentic sample of cimifugin by m m p and IR, MS spectral comparisons

The second new compound (**4**) $C_{15}H_{16}O_6$, m p 191°, $[\alpha]_D$ + 49° showed positive $FeCl_3$ color test and characteristic UV[λ_{max}^{MeOH} 231, 251, 257 (inf), 299 nm] The NMR spectrum of **4** was almost identical with that of cimifugin (**3**), but the signal of methoxyl group (4 06) in **3** was replaced by that of a phenolic hydroxyl group (12 76) in **4** In addition to this, the fact that methylation of 4 gave cimifugin (**3**) proved **4** to be 4-desmethyl cimifugin and therefore it was designated as norcimifugin

The third new compound (**5**) $C_{13}H_{10}O_6$, m p 242° (dec) showed positive $FeCl_3$ color test and very similar UV absorption to those of 4-desmethyl khellin[6] The NMR spectrum indicated the presence of a methoxyl group (3 77, 3H, s), a hydroxymethyl group (a methylene group 4 35 2H, s, a hydroxyl group 5 60), an olefinic proton on the γ-pyrone ring

[4] Chemical shifts are given in ppm from the internal standard TMS in DMSO-d_6 at 100 MHz Coupling constants in Hz

[5] Since the C-6 proton signal (6 05 ppm, *d*, *J* 1), coupled with C-7 methyl group (2 37 ppm, *d*, *J* 1) was observed in the NMDR spectrum while the C-8 aromatic proton signal was absent iodine located at C-8 in the dihydrofurochromone skeleton of **9**

[6] BENCZE W EISENBEISS J and SCHMID, H (1956) *Helv Chim Acta* **39**, 923

[7] KONDO, Y and TAKEMOTO T (1972) *Chem Pharm Bull* **20**, 1940

(6 05, 1H, *s*), two protons on the furan ring (7 05, 1H, *d*, *J* 2, 7 95, 1H, *d*, *J* 2) and a chelated hydroxyl group (10 10) In comparison with the NMR spectrum of khellol (**1**), the absence of a proton signal on the benzene ring at 7 20–7 33 ppm region in the spectrum of **5** suggested that oxygen functions located at both positions C-4 and C-8 in the furochromone structure of **5** From these findings **5** was deduced to be 4-desmethyl ammiol and hence it was named as norammiol

EXPERIMENTAL

Extraction and isolation procedure Fresh leaves and stems (1 85 kg) were extracted with MeOH The filtered MeOH extract was concentrated to a small vol, washed repeatedly with *n*-hexane, and taken up in EtOAc The EtOAc solution was shaken with H_2O, dried and concentrated to a syrup which was dissolved in $CHCl_3$ and poured on a column of silica gel (300 g) Elution with $CHCl_3$ and increasing amount of Me_2CO in $CHCl_3$ afforded the following fractions each of which was examined by TLC [silica gel G, $CHCl_3$–Me_2CO, 1 1] (a) Norkhellol (**2**), eluted with $CHCl_3$–Me_2CO (10 1), a colorless needles (200 mg) from MeOH–THF, m p 200–202° IR ν_{max}^{KBr} 3360, 1660, 1625, 1590 cm^{-1} NMR (δ in DMSO-d_6) 4 40 (2H, *d*, *J* 6), 5 80 (1H, *t*, *J* 6, OH), 6 28 (1H, *s*), 7 03 (1H, *d*, *J* 3), 7 20 (1H, *s*), 7 95 (1H, *d*, *J* 3), 13 35 (1H s, OH) UV λ_{max}^{MeOH} nm (ϵ) 245 (37 700), 253 (43 500), 262 (inf 29 600), 285 (inf 6400) MS (*m/e*) 232 (M^+) (b) Norcimifugin (**4**), eluted with $CHCl_3$–Me_2CO (8 1), m p 191–192° (930 mg) from MeOH IR ν_{max}^{KBr} 3250 (br), 1665, 1625, 1595 cm^{-1} MS (*m/e*) 292 (M^+) (Found C, 61, 42, H, 5 58 $C_{15}H_{16}O_6$ requires C, 61 70, H, 5 52%) (c) Khellol (**1**), later fractions eluted with $CHCl_3$–Me_2CO (8 1), m p 175–176° (2 61 g) from MeOH (d) Norammiol (**5**), eluted with $CHCl_3$–Me_2CO (5 1), needles (130 mg) from MeOH–THF, m p 240–242° (dec) IR ν_{max}^{KBr} 3400–3100 (br), 1655, 1605 cm^{-1} MS (*m/e*) 262 (M^+) (Found C, 59 79, H, 4 01 $C_{13}H_{10}O_6$ requires C, 59 79, H, 3 85%) (e) Cimifugin (**3**), eluted with $CHCl_3$–Me_2CO (4 1), m p 128–130° (594 mg) from C_6H_6–Me_2CO which on recrystallization from aq MeOH gave needles m p and m m p 107°, identical IR and MS spectra with an authentic sample of cimifugin

Reduction of **3** To a solution of **3** in pyridine (153 mg/3 ml) mesyl chloride (63 mg) was added at 5° The mixture was kept for 12 hr at the temp and poured onto ice The aqueous phase was extracted repeatedly with CH_2Cl_2 The combined CH_2Cl_2 extracts were washed with 0 2 N HCl, aq $NaHCO_3$, saturated aq NaCl, dried (Na_2SO_4) and concentrated to give a resinous product which was purified by preparative TLC (silica gel, $CHCl_3$–MeOH, 100 1) An amorphous chloride (70 mg), MS (*m/e*) 326, 324 (M^+) was obtained A soln of the chloride (110 mg) and NaI (400 mg) in AcOH (5 ml) was refluxed for 16 hr The reaction mixture was poured into H_2O and extracted with CH_2Cl_2 The CH_2Cl_2 extract, after washing with aq $NaHCO_3$, 3% aq $Na_2S_2O_3$, aq NaCl and dried with Na_2SO_4, was concentrated to give a glass which was separated by preparative TLC (silica gel, C_6H_6–EtOAc, 1 1) The more mobile compound was an iodide (**9**) m p 147° (18 mg) from Et_2O IR $\nu_{max}^{CHCl_3}$ 3580, 3400, 1660, 1625, 1590 cm^{-1} MS (*m/e*) 401 (M^+) NMR (δ in $CDCl_3$) 1 21 (3H, *s*), 1 36 (3H, *s*), 1 90 (1H, br s, OH), 2 37 (3H, *d*, *J* 1), 3 24 (2H, *d*, *J* 8), 4 80 (1H, *t*, *J* 8), 6 05 (1H, *d*, *J* 1), 12 91 (1H, *s*, OH) UV λ_{max}^{MeOH} nm (ϵ) 216 (31 000), 233 (inf 21 700), 262 (20 100) (Found C, 44 59, H, 3 74, I, 31 63 $C_{15}H_{15}IO_5$ requires C, 44 93, H 3 77, I, 31 65%) The less mobile was a deoxy compound (**8**) m p 157–159° (61 mg) from EtOAc which was identical with an authentic sample of visamminol by m m p and IR, MS comparisons

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