Acta Chemica Scandinavica B 33 (1979) 400—404

Chemical Studies on Bryophytes. 22. Flavonoid *C*-Glycosides of *Mnium undulatum*

BENGT-GÖRAN ÖSTERDAHL

Institute of Chemistry, Organic Chemistry Department, University of Uppsala, Box 531, S-751 21, Sweden

Seven flavonoid *C*-glycosides have been isolated from the moss *Mnium undulatum* Hedw. [*Plagiomnium u.* (Hedw.) P. Kop.]. As well as saponarin, schaftoside, neoschaftoside, isoschaftoside, neoisoschaftoside and vicenin-2, a previously unknown 6,8-di-*C*-glycoside is reported: A chrysoeriol 6-*C*-arabinosyl-8-*C*-hexoside. ^{13}C NMR spectra of saponarin, schaftoside, isoschaftoside and vicenin-2 were measured and used for the structure determinations. The structures of the other three compounds were determined using UV, ^{1}H NMR, acid treatment and the MS of the permethyl ethers.

In 1967 Harborne reported the existence of flavone *C*-glycosides in *Mnium undulatum* Hedw. [*Plagiomnium u.* (Hedw.) P. Kop.].[1] Saponarin (isovitexin 7-*O*-β-D-glucopyranoside, *1*), one of the two main flavonoids in *Mnium u.*, has earlier been identified from the moss [2] and its structure confirmed by ^{13}C NMR spectroscopy.[3] A recently published report described the isolation of three flavonoid *C*-glycosides from the moss.[4] Besides saponarin (*1*), an apigenin 6,8-di-*C*-glycoside, with the same, or nearly the same, sugar units in the 6- and 8-positions, and a third flavonoid, which is probably vitexin 7-*O*-glucoside, were identified.[4]

The present paper reports the identification of six flavonoid *C*-glycosides in addition to saponarin (*1*) (Table 1). Five of the flavonoids, the other main component *2* and four of the minor compounds, are apigenin 6,8-di-*C*-glycosides (*3*, *4*, *5* and *6*), the sixth is a 6,8-di-*C*-glycoside of chrysoeriol (*7*). A few other apigenin and luteolin *C*-glycosides, in very small quantities, were also isolated from the moss, but no vitexin 7-*O*-glucoside could be detected.

None of the isolated flavonoids were hydrolyzed on acid treatment suggesting that they are *C*-glycosides. UV-visible spectral data of *2*, *3*, *4*, *5* and *6* indicated that the aglycone moiety is apigenin.[5] This was confirmed by ^{1}H NMR spectroscopy for *2*, *3* and *6*, which also indicated that they are 6,8-di-*C*-glycosides. Acid treatment of *2* gave a dominating Wessely-Moser product (*3*) and a few additional isomers suggesting that *2* has different sugar units in the 6- and 8-positions.

The ^{13}C NMR spectrum of *2* in DMSO-d_6 showed no signals in the interval 90.0 to 100.0 ppm where the C-6 and the C-8 resonances are always found in 5,7-dihydroxy flavonoids.[6] The signals found at 103.9 and 108.1 ppm are in accordance with those earlier reported for C-8 and C-6 in *C*-glycosylated flavonoids.[3,7,8] This confirmed that *2* is an apigenin 6,8-di-*C*-

Table 1. R_F values of the isolated flavonoid *C*-glycosides from *Mnium undulatum*.[a]

Compound	Solvent		
	15 % HOAc	50 % HOAc	TBA
1 Saponarin	0.53	0.80	0.35
2 Schaftoside	0.40	0.68	0.21
3 Isoschaftoside	0.29	0.62	0.13
4 Neoschaftoside	0.49	0.75	0.35
5 Neoisoschaftoside	0.14	0.53	0.15
6 Vicenin-2	0.35	0.64	0.19
7 Chrysoeriol 6-*C*-arabinosyl-8-*C*-hexoside	0.19	0.55	0.09

[a] R_F values on 0.1 mm pre-coated cellulose TLC plates.

0302-4369/79/060400-05$02.50

Table 2. ^{13}C NMR shifts of the sugar moieties of some of the isolated flavonoid *C*-glycosides.

Compound	Temp./°C	Glucose						Arabinose				
		C-1	C-2	C-3	C-4	C-5	C-6					
1 [a]	23	72.9 (101.5)	69.8 (74.0)	79.1 (76.1)	69.8 (71.2)	81.1 (77.4)	61.0 (61.0)					
2	80	73.3 [d]	70.5 [c]	78.4	70.0	81.0	60.7	74.8 [d]	74.3	70.8 [c]	68.9	68.5
3	23	73.3	70.7 [c]	78.9	70.5	82.0	61.4	74.3	74.0	70.9 [c]	69.6	68.6
6	80	73.4	70.8	78.7	70.0	81.4	61.0					
		74.3	71.5	78.7	69.6	81.2	60.7					
Isovitexin [b]	50	73.4	70.7	79.0	70.7	81.3	61.6					
Vitexin [b]	100	73.9	71.4	78.8	70.8	81.4	61.5					

[a] The values in parentheses are assigned for the 7-*O*-β-D-glucose unit. [b] Isovitexin and vitexin were isolated after acid treatment of *1*. [c] Assignment bearing the same superscript in any spectrum may be reversed. [d] Assigned for C-1 by selective decoupling.

glycoside. The sugar signals of *2* (Table 2) are identical with those reported for schaftoside (apigenin 6-*C*-β-D-glucopyranosyl-8-*C*-α-L-arabinopyranoside).[8] In Table 2 the assignments of the carbon signals in the glucose moiety are based on those recently published.[9] Thus, some of the earlier tentatively assigned chemical shifts have been reversed.[3] In order to determine the position of the sugar units, *2* was permethylated (PM). MS of PM *2* indicated a hexosyl unit in the 6-position and a pentosyl unit in the 8-position; the MS data are in agreement with those reported for schaftoside.[10] This established the structure of *2* as apigenin 6-*C*-β-D-glucopyranosyl-8-*C*-α-L-arabinopyranoside (schaftoside).

According to two-dimensional TLC data, compound *3* is the Wessely-Moser isomer of *2*. This was further indicated by the MS of the PM derivative of *3*. The results obtained were in good agreement with those reported for isoschaftoside.[10] Permethylation of *3* also gave a product derived from an impurity, in a very small amount, which was identified as a PM luteolin 6,8-di-*C*-hexoside according to MS data. The ^{13}C NMR spectrum of *3* in DMSO-d_6 is almost identical with the spectrum of *2*. Thus, the apigenin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-glucopyranoside structure can be assigned to compound *3*.

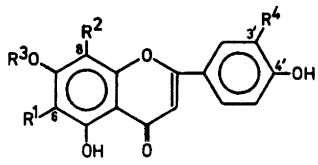
Acid treatment of *4* and *5* for 60 min gave a nearly complete isomerization to schaftoside (*2*) and isoschaftoside (*3*), respectively, which gradually rearranged through a Wessely-Moser-rearrangement. Thus *2*, *3*, *4* and *5* are interconvertible by acid treatment. Similar isomerizations have been observed previously with this group of compounds,[11–13] possibly due to pyranose – furanose isomerization.[10–13]

The MS data of PM *4* are in agreement with those reported for PM neoschaftoside.[10,11] Considering these data, *4* is given the structure apigenin 6-*C*-β-D-glucosyl-8-*C*-α-L-arabinoside (neoschaftoside).

MS of PM *3* (isoschaftoside) and PM *5* are identical. Since *5* yields *2*, *3* and *4* by acid treatment, the proposed structure of *5* is apigenin 6-*C*-α-L-arabinosyl-8-*C*-β-D-glucoside (neoisoschaftoside).

Compound *6* gave no Wessely-Moser-rearrangement during acid treatment, indicating that *6* has the same, or very similar, sugar units in the 6- and 8-positions. The MS of PM *6* is identical to that of PM apigenin 6,8-di-*C*-β-D-glucopyranoside.[3,10] It is, however, not possible to decide the structure of the sugar units by MS, although this is feasible using ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum of *6* in DMSO-d_6 the sugar signals (Table 2) correspond well to those earlier reported for apigenin 6,8-di-*C*-β-D-glucopyranoside isolated from *Hedwigia ciliata*.[3] Co-chromatography with this sample confirms that the structure of *6* is apigenin 6,8-di-*C*-β-D-glucopyranoside (vicenin-2).

UV-visible data of *7* indicated that the aglycone moiety is a luteolin derivative substituted in the 3′-position.[5] ^1H NMR spectroscopy of *7* in DMSO-d_6 confirmed that *7* is a chrysoeriol (3′-*O*-methylluteolin) 6,8-di-*C*-glycoside. Upon



	R^1	R^2	R^3	R^4
1	β-D-glucopyranosyl	H	β-D-glucopyranosyl	H
2	β-D-glucopyranosyl	α-L-arabinopyranosyl	H	H
3	α-L-arabinopyranosyl	β-D-glucopyranosyl	H	H
4	β-D-glucosyl	α-L-arabinosyl	H	H
5	α-L-arabinosyl	β-D-glucosyl	H	H
6	β-D-glucopyranosyl	β-D-glucopyranosyl	H	H
7	arabinosyl	hexosyl	H	OCH_3

acid treatment of *7*, a Wessely-Moser isomer was formed indicating that the two sugar units in the 6- and 8-positions are different. MS of the perdeuteriomethylated (PDM) *7* showed M+ at *m/e* 764 corresponding to the molecular weight of PDM 6,8-*C*-hexosyl-*C*-pentosylchrysoeriol. The sugar in the 6-position of 6,8-di-*C*-glycosylflavones is more easily fragmented.[10] In the MS of PDM *7* the peaks M-137 (*m/e* 627) and M-126 (*m/e* 638) are dominant and both derive from a *C*-pentosyl unit. The peak intensities; M − 137 > M − 126 > M − 154, indicated an arabinosyl unit.[10] From these MS data it can be concluded that *7* is chrysoeriol 6-*C*-arabinosyl-8-*C*-hexoside. It was not possible to decide the structure of *7* more precisely because of the small amount of sample available.

EXPERIMENTAL

UV-visible and ^{13}C NMR spectra were recorded as described earlier.[3] Chemical shifts were referred to external TMS on the basis of the chemical shift of DMSO-d_6 (39.5 ppm). ^1H and ^{13}C NMR spectra were determined at 80 °C with a Jeol FX-100 FT spectrometer. Mass spectra were recorded on an LKB 9000 and the optical rotations were measured on a Perkin Elmer 241 Polarimeter. Solvent systems: BuOH − HOAc − H_2O, 6:1:2 (BAW), *t*-BuOH − HOAc − H_2O, 3:1:1 (TBA), $CHCl_3$ − CH_3COCH_3, 3:1 (CA).

Isolation. The moss was collected in the surroundings of Uppsala. The air-dried material was pulverized and extracted several times with 80 % aqueous MeOH at room temperature. The methanolic extract was evaporated in vacuum and the residue was washed with ether. Gel filtration on a Sephadex G-25 column with 70 % aqueous MeOH gave a crude flavone fraction. Repeated PC on Whatman 3MM paper with BAW and 15 % HOAc and CC on cellulose with 5 % HOAc of the crude flavone fraction gave a complete separation of the flavone *C*-glycosides. R_F values, see Table 1.

Acid treatment was performed with 6 % HCl for 5 − 8 h at 100 °C and the products were identified by 2-dimensional TLC in 15 % HOAc and TBA.

The permethyl (perdeuteriomethyl) ethers were prepared with NaH, DMSO and CH_3I (CD_3I) according to Hakomori's procedure.[14] The permethyl (perdeuteriomethyl) ethers were purified by TLC on silica gel with $CHCl_3$ − CH_3COCH_3 (3:1) as eluent.

Apigenin 6-C-β-D-glucopyranosyl 7-O-β-D-glucopyranoside (isovitexin 7-*O*-β-D-glucopyranoside, saponarin, *1*), > 280 mg, R_F values, see Table 1. *UV* (99.9 % MeOH): 271, 332; (+$AlCl_3$): 278, 301, 351, 380sh; (+$AlCl_3$/HCl): 279, 300, 347, 380sh; (+MeONa): 257sh, 269, 390; (+NaOAc): 258sh, 269, 391; (+NaOAc/-H_3BO_3): 270, 338 nm. ^1H *NMR* (100 MHz, DMSO-d_6): δ 7.92 (H2′ and H6′, d, *J* 9 Hz), 6.95 (H3′ and H5′, d, *J* 9 Hz), 6.88 (H8, s), 6.79 (H3, s), 5.1 − 3.1 (sugar H). ^{13}C *NMR* (100 MHz, DMSO-d_6): δ 182.1 (C-4), 164.2 (C-2), 162.5 (C-7), 161.4 (C-5), 159.4 (C-4′), 156.5 (C-8a), 128.7 (C-2′ and C-6′), 121.0 (C-1′), 116.1 (C-3′ and C-5′), 110.6 (C-6), 104.9 (C-4a), 103.3 (C-3), 93.8 (C-8), sugar C, see Table 2. *Acid hydrolysis* of *1* gave glucose and isovitexin, treatment of *1* with 6 % HCl for 7 − 8 h gave also vitexin. ^{13}C NMR of isovitexin and vitexin, see Table 2. *1 permethyl ether* (PM *1*). R_F value: 0.25 (CA). *MS* [70 eV, 135 °C; *m/e* (% rel. int.)]: 734 (24), 730 (14), 719 (20), 704 (24), 703 (64), 673 (11), 629 (10), 571 (14), 559 (22), 516 (12), 515 (35), 502 (12), 501 (42), 499 (24), 486 (30), 485 (100), 484 (20), 483 (30), 471 (16), 469 (26), 454 (27), 453 (87), 451 (12), 439 (15), 411 (13), 397 (10), 383 (10), 381 (20), 379 (13), 369 (13), 367 (17), 365 (12), 356 (13), 355 (60), 354 (11), 353 (47), 351 (12), 342 (17), 341 (76), 339 (19), 337 (11), 327 (20), 325 (23), 323 (26), 311 (17), 310 (11), 309 (18). Only peaks larger than 10 % of the base peak are given.

Apigenin 6-C-β-D-*glucopyranosyl-8*-C-α-L-*arabinopyranoside* (schaftoside, *2*) 320 mg, m.p. 224–226 °C, $[\alpha]_D^{21}$ +131 ° (*c* = 0.087, H_2O). R_F values, see Table 1. *UV* (99.9 % MeOH): 272, 333; (+$AlCl_3$): 264sh, 279, 305, 352, 384sh; (+$AlCl_3$/HCl): 264sh, 280, 304, 348, 384sh; (+MeONa): 282, 333, 400; (+NaOAc): 282, 312sh, 337, 395; (+NaOAc/H_3BO_3): 277sh, 283, 320, 349, 400sh nm. ^1H *NMR* (100 MHz, DMSO-d_6): δ 8.05 (H2′ and $H_{6'}$, d, *J* 9 Hz), 6.92 (H3′ and H5′, d, *J* 9 Hz), 6.71 (H3, s) 4.80 (glycose H1, *J* 10 Hz), 4.75 (glycose H1, *J* 9.5 Hz), 4.2–3.2 (sugar H). ^{13}C *NMR* (100 MHz, DMSO-d_6): δ 181.9 (C-4), 163.7 (C-2), 161.7 (C-7), 160.8 (C-5), 159.2 (C-4′), 154.0 (C-8a), 128.6 (C-2′ and C-6′), 121.1 (C-1′), 115.7 (C-3′ and C-5′), 108.1 (C-6), 103.9 (C-8), 103.3 (C-4a), 102.1 (C-3), sugar C, see Table 2. *Acid treatment* of *2* with 6 % HCl for 7 h gave *3* as the main component, small amounts of *4*, *5* and a few degradation products. *2 permethyl ether* (PM *2*). R_F value: 0.26 (CA). *MS* [70 eV, 125 °C; *m/e* (% rel. int.)]: 705 (6), 704 (16), 690 (9), 689 (27), 675 (12), 674 (39), 673 (100), 657 (9), 641 (6), 602 (5), 601 (14), 573 (10), 571 (7), 553 (5), 543 (10), 542 (12), 541 (38), 530 (16), 529 (52), 527 (7), 515 (9), 513 (7), 511 (6), 499 (8), 497 (11), 485 (5). Only peaks larger than 5 % of the base peak are given. *2 perdeuteriomethyl ether* (PDM *2*). R_F value: 0.20 (CA). *MS* [70 eV, 110 °C; *m/e* (% rel. int.)]: 734 (16), 717 (26), 716 (29), 702 (31), 701 (83), 700 (100), 699 (18), 682 (8), 625 (14), 597 (18), 564 (9), 562 (12), 561 (35), 551 (22), 550 (77), 549 (10), 533 (10), 514 (10). Only peaks larger than 8 % of the base peak are given.

Apigenin 6-C-α-L-*arabinopyranosyl-8*-C-β-D-*glucopyranoside* (isoschaftoside, *3*), 25 mg, $[\alpha]_D^{25}$ +51 ° (*c* = 0.56, H_2O). R_F values, see Table 1. *UV* (99.9 % MeOH): 272, 336; (+$AlCl_3$): 262sh, 279, 304, 355, 388sh; (+$AlCl_3$/HCl): 262sh, 279, 303, 351, 388sh; (+MeONa): 282, 335sh, 404; (+NaOAc): 282, 314sh, 398; (+NaOAc/H_3BO_3): 273, 285sh, 326, 340, 410sh nm. ^1H *NMR* (100 MHz, DMSO-d_6): δ 7.96 (H2′ and H6′, d, *J* 8 Hz), 6.93 (H3′ and H5′, d, *J* 8 Hz), 6.71 (H3, s) 4.84 (glycose H1, d, *J* 11 Hz), 4.72 (glycose H1, d, *J* 9.5 Hz), 4.2–3.0 (sugar H). ^{13}C *NMR* (100 MHz, DMSO-d_6): δ 182.0 (C-4), 163.8 (C-2), 161.1 (C-7), 160.9 (C-5), 158.4 (C-4′), 154.8 (C-8a), 128.5 (C-2′ and C-6′), 121.4 (C-1′), 115.7 (C-3′ and C-5′), 108.0 (C-6), 104.4 (C-8), 102.9 (C-4a), 102.4 (C-3), sugar C, see Table 2. *Acid treatment* of *3* with 6 % HCl for 8½ h gave *2* as the main component, besides small amounts of *4*, *5* and a few degradation products. *3 permethyl ether* (PM *3*). R_F value: 0.21 (CA). *MS* [70 eV, 95 °C; *m/e* (% rel. int.)]: 704 (19), 689 (22), 675 (22), 674 (80), 673 (100), 657 (9), 645 (8), 643 (17), 641 (6), 617 (5), 585 (24), 573 (33), 571 (5), 559 (13), 543 (5), 541 (8), 529 (10), 499 (5). Only peaks larger than 5 % of the base peak are given.

Apigenin 6-C-β-D-*glucosyl-8*-C-α-L-*arabinoside* (neoschaftoside, *4*), 11 mg. R_F values, see Table 1. *UV* (99.9 % MeOH): 272, 333; (+$AlCl_3$): 263sh, 279, 304, 352, 384sh; (+$AlCl_3$/HCl): 263sh, 279, 303, 349, 384sh; (+MeONa): 282, 335, 398; (+NaOAc): 282, 312sh, 338sh, 394; (+NaOAc/H_3BO_3): 273, 285sh, 324, 341, 410sh nm. *Acid treatment* of *4* with 6 % HCl for 60 min gave *2*, further treatment with 6 % HCl gave *3* and *5*. *4 permethyl ether* (PM *4*). R_F value: 0.27 (CA). *MS* [70 eV, 90 °C; *m/e* (% rel. int.)]: 705 (7), 704 (18), 690 (10), 689 (28), 675 (10), 674 (37), 673 (100), 657 (10), 601 (15), 573 (13), 571 (8), 543 (11), 542 (12), 541 (36), 530 (19), 529 (55), 515 (15), 513 (8), 499 (18), 497 (11), 485 (11), 483 (11). Only peaks larger than 8 % of the base peak are given.

Apigenin 6-C-α-L-*arabinosyl-8*-C-β-D-*glucoside* (neoisochaftoside, *5*), 15 mg, $[\alpha]_D^{24}$ −11 ° (*c* = 0.62, H_2O). R_F values, see Table 1. *UV* (99.9 % MeOH): 272, 306sh, 334; (+$AlCl_3$): 262sh, 268sh, 279, 306, 355, 390sh; (+$AlCl_3$/HCl): 261sh, 268sh, 279, 305, 351, 390sh; (+MeONa): 282, 316sh, 397; (+NaOAc): 281, 306sh, 384; (+NaOAc/H_3BO_3): 274, 310, 322sh, 342 nm. *Acid treatment* of *5* with 6 % HCl for 60 min gave *3*, further treatment with 6 % HCl gave *2* and *4*. *5 permethyl ether* (PM *5*). R_F value: 0.28 (CA). *MS* [70 eV, 90 °C; *m/e* (% rel. int.)]: 704 (19), 689 (18), 675 (11), 674 (35), 673 (100), 657 (13), 645 (10), 643 (16), 615 (8), 586 (9), 585 (26), 574 (18), 573 (55), 560 (8), 559 (22), 543 (8), 541 (13), 530 (8), 529 (16), 515 (16). Only peaks larger than 8 % of the base peak are given.

Apigenin 6,8-di-C-β-D-*glucopyranoside* (vicenin-2, *6*) 20 mg. R_F values, see Table 1. *UV* (99.9 % MeOH): 272, 335; (+$AlCl_3$): 263sh, 279, 305, 350, 384sh; (+$AlCl_3$/HCl): 263sh, 279, 304, 348, 384sh; (+MeONa): 282, 333, 400; (+NaOAc): 281, 336, 397; (+NaOAc/H_3BO_3): 274, 284sh, 322, 351, 420sh nm. ^1H *NMR* (100 MHz, DMSO-d_6): δ 7.95 (H2′ and H6′, d, *J* 9 Hz), 6.93 (H3′ and H5′, d, *J* 9 Hz), 6.70 (H3, s), 4.83 (glucose H1, d, *J* 10 Hz), 4.66 (glucose H1, d, *J* 10 Hz), 4.1–3.1 (sugar H). ^{13}C *NMR* (100 MHz, DMSO-d_6): δ 181.8 (C-4), 163.7 (C-2), 161.3 (C-7), 160.8 (C-5), 159.2 (C-4′), 154.6 (C-8a), 128.4 (C-2′ and C-6′), 121.3 (C-1′), 115.6 (C-3′ and C-5′), 108.0 (C-6), 104.4 (C-4a), 103.4 (C-8), 102.3 (C-2), sugar C, see Table 2. No isomerization was observed during *acid treatment* of *6* with 6 % HCl. *6 permethyl ether* (PM *6*). R_F value: 0.27 (CA). *MS* [70 eV, 95 °C; *m/e* (% rel. int.)]: 749 (10), 748 (21), 734 (11), 733 (29), 719 (11), 718 (39), 717 (100), 701 (11), 645 (23), 615 (10), 587 (15), 586 (15), 585 (45), 575 (10), 574 (23), 573 (65), 571 (11), 559 (13), 557 (12), 555 (12), 543 (16), 541 (25), 530 (12), 527 (11). Only peaks larger than 10 % of the base peak are given. *6 perdeuteriomethyl ether* (PDM *6*). R_F value: 0.24 (CA). *MS* [70 eV, 110 °C; *m/e* (% rel. int.)]: 781 (21), 764 (26), 763 (28), 749 (26), 748 (83), 747 (100), 746 (21), 729 (8), 673 (10), 672 (16), 611 (9), 609 (15), 608 (38),

598 (31), 597 (93), 596 (14), 592 (9), 580 (12). Only peaks larger than 8 % of the base peak are given.

Chrysoeriol 6-C-arabinosyl-8-C-hexoside (7), 2 mg. R_F values, see Table 1. *UV* (99.9 % MeOH): 253, 272, 344; (+$AlCl_3$): 262, 279, 299, 362, 392sh; (+$AlCl_3$/HCl): 262, 279, 299, 359, 392sh; (+MeONa): 268, 282, 340sh, 410; (+NaOAc): 279, 323, 402; (+NaOAc/H_3BO_3): 273, 282sh, 335, 410sh nm. ^1H *NMR* (100 MHz, DMSO-d_6): δ 7.62 (H6′, q, J 9 Hz and 2 Hz), 7.53 (H2′, d, J 2 Hz), 6.91 (H5′, d, J 9 Hz), 6.72 (H3, s) 4.85 (glycosyl H1, d, J 10 Hz), 4.65 (glycosyl H1, d, 10 Hz), 4.3 – 2.8 (sugar H), 3.90 (–OCH_3, s). *Acid treatment* of 7 with 6 % HCl for 5 h gave an isomerization product with R_F values: 0.30 (15 % HOAc) and 0.16 (TBA) on cellulose TLC plates. *7 perdeuteriomethyl ether* (PDM 7). R_F value: 0.23 (CA). *MS* [70 eV, 90 °C; *m/e* (% rel. int.)]: 765 (10), 764 (23), 747 (12), 746 (29), 732 (12), 731 (38), 730 (100), 712 (9), 701 (17), 700 (38), 699 (11), 639 (12), 638 (31), 628 (18), 627 (58), 626 (10), 610 (19), 597 (11), 591 (12), 581 (11), 580 (27). Only peaks larger than 9 % of the base peak are given.

Acknowledgements. I wish to thank Professor Gerd Bendz for stimulating discussions. I am also indebted to Professor Arne Fredga for his interest in this work and Docent Olle Mårtensson for making the species determination. For technical assistance in part of the isolation work I am indebted to Fil.kand. Kjell Magnusson. Support from the Swedish Natural Science Research Council (Prof. G. Bendz) is gratefully acknowledged.

REFERENCES

1. Harborne, J. B. *Comparative Biochemistry of the Flavonoids*, Academic, London 1967.
2. Nilsson, E. *Unpublished work.*
3. Österdahl, B.-G. *Acta Chem. Scand. B 32* (1978) 93.
4. Vandekerkhove, O. *Z. Pflanzenphysiol. 86* (1978) 135.
5. Mabry, T. J., Markham, K. R. and Thomas, M. B. *The Systematic Identification of Flavonoids*, Springer, Berlin 1970.
6. Wagner, H., Chari, V. M. and Sonnenbichler, J. *Tetrahedron Lett.* (1976) 1799.
7. Hostettmann, K. and Jacot-Guillarmod, A. *Helv. Chim. Acta 59* (1976) 1584.
8. Chopin, J., Dellamonica, G., Besson, E., Skrzypczakowa, L., Bubzianowski, J. and Mabry, T. J. *Phytochemistry 16* (1977) 1999.
9. Chari, V. M., Wagner, H., Schilling, G. and Nesmélyi, A. *11th IUPAC International Symposium on Chemistry of Natural Products*, Bulgaria 1978, Vol. 2, p. 279.
10. Bouillant, M.-L., Favre-Bonvin, J. and Chopin, J. *Phytochemistry 14* (1975) 2267.
11. Markham, K. R., Porter, L. J., Campbell, E. O., Chopin, J. and Bouillant, M.-L. *Phytochemistry 15* (1976) 1517.
12. Chopin, J., Bouillant, M.-L., Wagner, H. and Galle, K. *Phytochemistry 13* (1974) 2583.
13. Prolic, A., Raynaud, J., Combier, H., Bouillant, M.-L. and Chopin, J. *C. R. Acad. Sci. Ser. D 277* (1973) 2813.
14. Hakomori, S. *J. Biochem (Tokyo) 55* (1964) 205.

Received February 19, 1979.