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DI-*C*-GLYCOSYLFLAVONES FROM *CRATAEGUS MONOGYNA*

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Key Word Index—*Crataegus monogyna*; Rosaceae; 6,8-di-*C*-glycosylflavones; vicenin-2; vicenin-1; vicenin-3; schaftoside; isoschaftoside; neoschaftoside; neoisoschaftoside.

Abstract—Six di-*C*-glycosylapigenins have been characterized in leaves of *Crataegus monogyna*: vicenins-1, -2 and -3; schaftoside; iso-, neo- and neoiso-schaftoside. This study corrects a previous misidentification of the flavonoid constituents of this tissue.

In a previous study of the leaf flavonoids of *Crataegus monogyna* Jacq., two compounds were isolated which were considered to be rotational isomers of 6,8-di-*C*-glucosylapigenin from their chemical degradations, UV spectra and acid isomerization [1]. In the present reinvestigation of the leaf tissue of this plant we have shown the presence of a complex mixture of 6,8-di-*C*-glycosylapigenins which have been identified by permethylation and mass spectrometry in comparison with known compounds.

The mixture of di-*C*-glycosylflavonoids was isolated from the water-soluble fraction after previous extraction with chloroform and butanol. Successive polyamide column chromatography (CC) in 90% EtOH and H_2O, followed by PPC in BAW gave a mixture, which was fractionated by PPC in 15% HOAc and BAW. The lower band in 15% HOAc gave compounds **1** and **5** and the higher band gave compounds **2**, **3** and **4**. All of these constituents showed the same UV spectrum and diagnostic shifts [2] as apigenin, none of them was modified by alkaline hydrolysis, and all except **2** were isomerized by acid hydrolysis. Permethylation of **1** and TLC gave one main band which showed the MS of a PM 6-*C*-arabinosyl-8-*C*-hexosylapigenin (M^+ 704, M − 131 > M − 175, M − 131 > M − 119 > M − 145) [3] with the same R_f as PM isoschaftoside (PM 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-glucopyranosylapigenin). **1** and isoschaftoside co-chromatographed. PC and co-PC of **5** in 2% HOAc showed it to be a mixture of isoschaftoside and neoisoschaftoside [4]. Permethylation of **2** and TLC gave one main band; however, the MS showed the presence of a mixture containing a PM 6,8-di-*C*-hexosylapigenin (M^+ 748) and PM *C*-hexosyl-*C*-pentosylapigenins (M^+ 704), which were identified as PM vicenin-2 (PM 6,8-di-*C*-β-D-glucopyranosylapigenin), PM vicenin-1 (PM 6-*C*-β-D-xylopyranosyl-8-*C*-β-D-glucopyranosylapigenin) and PM vicenin-3 (PM 6-*C*-β-D-glucopyranosyl-8-*C*-β-D-xylopyranosylapigenin) by co-chromatography. Co-chromatography of **2** and vicenin-2 showed them to be identical. Permethylation of **3** and TLC gave one main band which agreed with the MS of a PM 6-*C*-hexosyl-8-*C*-pentosylapigenin (M^+ 704, M − 175 > M − 131) and had the same R_f as PM schaftoside (PM 6-*C*-β-D-glucopyranosyl-8-*C*-α-L-arabinopyranosylapigenin). Co-chromatography of **3** and schaftoside showed them to be identical. Permethylation of **4** and TLC gave two bands. The lower band gave the MS a mixture containing a PM 6-*C*-hexosyl-8-*C*-pentosylapigenin (M^+ 704, M − 175 > M − 131) migrating like PM schaftoside and a PM 6-*C*-hexosylapigenin 2″-*O*-deoxyhexoside (M^+ 704, important peaks at 515, 499 and 341) [5]. The higher band gave the MS of a PM 6-*C*-hexosyl-8-*C*-pentosylapigenin (M^+ 704, M − 175 > M − 131) and the same R_f as PM neoschaftoside [3]. It follows from the above data that the methanolic leaf extract of *Crataegus monogyna* contains a mixture of di-*C*-glycosylapigenins with *C*-glucosyl, *C*-arabinosyl and *C*-xylosyl residues, namely: vicenin-2, vicenin-1, vicenin-3, schaftoside, isoschaftoside, neoschaftoside and neoisoschaftoside.

EXPERIMENTAL

Plant material. Leaf material was collected near Sofia (Vitosha Mountain, May 1978) and a voucher specimen, number 5030, is deposited in the Herbarium, Department of Pharmacognosy and Botany, Faculty of Pharmacy, Medical Academy, Sofia.

Isolation. Finely powdered, dried leaves (10 kg) were Soxhlet-extracted with MeOH (25 l.). The MeOH extract was concd, hot H_2O added, allowed to stand for 24 hr, filtered and the filtrate (6 l.) extracted with $CHCl_3$ (3 × 2 l.) and *n*-BuOH (6 × 3 l.). The aq. layer was concd to 800 ml and chromatographed on a polyamide column in 90% EtOH and H_2O successively. PPC of the flavonoid mixture (20 g) in BAW (4:1:2) and in 15% HOAc led to two fractions: R_f 0.30–0.43 and 0.46–0.55, respectively. PPC of the former in 15% HOAc gave **1** (R_f 0.42–0.45) and **5** (R_f 0.32–0.36). PPC of the latter fraction in BAW (4:1:2) gave **2** (R_f 0.19–0.22), **3** (R_f 0.26–0.29) and **4** (R_f 0.30–0.34).

1 (*isoschaftoside*). Yellow, crystalline powder (aq. MeOH, 100 mg); mp 230–232° (uncorr.); PC, R_f 0.23 (BAW 4:1:2), 0.43 (15% HOAc); UV λ_{max} 275, 336 (MeOH); 282, 306, 355, 386 ($AlCl_3$); 281, 304, 348, 385 ($AlCl_3$ + HCl); 282, 336, 388 (+NaOAc); 278, 338 (+NaOAc + H_3BO_3); 284, 335, 402 (+NaOMe). PM ether: Si gel TLC, R_f 0.20 ($CHCl_3$–EtOAc–Me_2CO, 5:4:1); MS *m/z* (%) 704 (M^+, 14), 689 (M − 15, 33), 673 (M − 31, 100), 657 (M − 47, 15), 643 (M − 61, 27), 585 (M − 119, 41), 573 (M − 131, 54), 559 (M − 145, 21), 541 (M − 163, 15) 529 (M − 175, 21), 515 (M − 189, 4).

2 (*vicenin*-2 + *vicenin*-1 + *vicenin*-3). Yellow, amorphous powder (MeOH, 80 mg); mp 225–230° (uncorr.); PC, R_f 0.21 (BAW 4:1:2), 0.49 (15% HOAc); UV λ_{max} (see **1**). PM ether: Si gel TLC, R_f 0.38 ($CHCl_3$–EtOAc–Me_2CO, 5:4:1); MS *m/z* (%) 748 (M_1^+, 18), 733 (M_1 − 15, 33), 717 (M_1 − 31, 100), 704 (M_2^+, 20), 701 (M_1 − 47, 16), 689 (M_2 − 15, 22), 685 (M_1 − 63, 11), 673 (M_2 − 31, 84), 657 (M_2 − 47, 13), 645 (M_1 − 103, 22), 643 (M_2 − 61, 22), 585 (M_1 − 163, M_2 − 119, 64), 573 (M_1 − 175, M_2 − 131, 98), 559 (M_1 − 189, M_2 − 145, 29), 543 (M_1 − 205, M_2 − 161, 20), 541 (M_1 − 207, M_2 − 163, 24), 529 (M_1 − 219, M_2 − 175, 22).

3 (*schaftoside*). Yellow amorphous powder (MeOH, 85 mg); mp 226–228° (uncorr.); PC, R_f 0.28 (BAW 4:1:2), 0.52 (15% HOAc); UV λ_{max} (see **1**). PM ether: Si gel TLC, R_f 0.28 ($CHCl_3$–EtOAc–Me_2CO, 5:4:1); MS, *m/z* (%) 704 (M^+, 31), 689 (M − 15, 35), 673 (M − 31, 100), 601 (M − 103, 25), 585 (M − 119, 19), 573 (M − 131, 25), 541 (M − 163, 40), 529 (M − 175, 50), 515 (M − 189, 27).

4 (*neoschaftoside* + *schaftoside* + 6-C-*hexosylapigenin* 2″-O-*deoxyhexoside*). Yellow amorphous powder (EtOH, 15 mg); PC, R_f 0.32 (BAW 4:1:2) 0.53 (15% HOAc); UV λ_{max} (see **1**). Permethylation and TLC on Si gel gave two bands R_f 0.28 (1) and 0.32 (2). MS (1), *m/z* (%) 704 (M^+, 15), 689 (M − 15, 32), 673 (M − 31, 100), 659 (M − 45, 20), 601 (M − 103, 17), 585 (M − 119, 15), 573 (M − 131, 27), 559 (M − 145, 21), 541 (M − 163, 37), 529 (M − 175, 46), 515 (M − 189, 45), 499 (M − 205, 51), 341 (66). MS (2), *m/z* (%) 704 (M^+, 22), 689 (M − 15, 30), 673 (M − 31, 100), 659 (M − 45, 12), 601 (M − 103, 15), 573 (M − 131, 25), 559 (M − 145, 10), 541 (M − 163, 35), 529 (M − 175, 42), 515 (M − 189, 15).

5 (*isoschaftoside* + *neoisoschaftoside*). Yellow amorphous powder (MeOH); PC, R_f 0.22 (BAW 4:1:2), 0.33 (15% HOAc); UV λ_{max} (see **1**). PC (2% HOAc) R_f 0.22 (isoschaftoside) and 0.10 (neoisoschaftoside).

REFERENCES

1. Nikolov, N. and Vodenicharov, R. (1975) *Khim. Prir. Soedin* **11**, 423.
2. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*. Springer, Berlin.
3. Bouillant, M. L., Favre-Bonvin, J. and Chopin, J. (1975) *Phytochemistry* **14**, 2267.
4. Österdahl, B. G. (1979) *Acta Chem. Scand.* **33**, 400.
5. Bouillant, M. L., Besset, A., Favre-Bonvin, J. and Chopin, J. (1978) *Phytochemistry* **17**, 527.

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TODDALIDIMERINE, A DIMERIC BENZOPHENANTHRIDINE ALKALOID FROM *TODDALIA ASIATICA**

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Key Word Index—*Toddalia asiatica*; Rutaceae; roots; dimeric benzophenanthridine alkaloid; toddalidimerine; dihydrochelerythrine; 8-acetonyldihydrochelerythrine; structural analysis.

Abstract—Toddalidimerine, a new dimeric benzophenanthridine alkaloid, has been isolated from the roots of *Toddalia asiatica*. On the basis of spectral analysis it has been characterized as 1,3-(8-hydrochelerythrinyl-8′-hydro-*N*-norchelerythrinyl) acetone. The presence of dihydrochelerythrine and 8-acetonyldihydrochelerythrine has been confirmed in this plant.

INTRODUCTION

The isolation of corynolamine and bocconoline [1] offered circumstantial evidence to the biogenetic introduction of a carbon unit at C-8 of the benzophenanthridine nucleus. This postulation received further support from the discovery of three dimeric bases, *meso*-1,3-bis(8-hydrosanguinarinyl) acetone (chelidimerine) (**1**) [2], its optically active isomer (sanguidimerine) [3] and 1,3-bis(8-hydrochelerythrinyl) acetone (**2**) [4], each comprising two similar monomeric units. In the present study the isolation of the first benzophenanthridine dimer with dissimilar component units from *Toddalia asiatica* further sustains the above observations. Evidence is presented in this communication for the characterization of the dimer as 1,3-(8-hydrochelerythrinyl-8′-hydro-*N*-norchelerythrinyl) acetone (**3**).

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