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HOSLOPPIN, A NEW PYRONE-SUBSTITUTED FLAVONOID FROM *HOSLUNDIA OPPOSITA*

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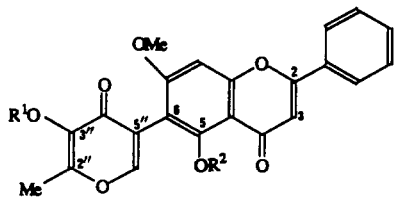
ABSTRACT.—Hosloppin [**1**], a new pyrone-substituted flavonoid, was isolated from the MeOH extract of the leaves of *Hoslundia opposita*. The structure of **1** was established as 3″-*O*-demethylhoslundin from an analysis of its spectroscopic data.

Hoslundia opposita Vahl (Lamiaceae) is known to contain a number of volatile constituents (1) and abietane-type esters (2). We previously reported the isolation and characterization of five new flavonoids (3,4) in addition to five known pentacyclic triterpenoids and one known flavonoid (4), from the twigs of *H. opposita* collected from two different places, Yaoundé and Bertoua, both in Cameroon. Examination of the MeOH extract of the leaves of this plant collected from Yaoundé has led to the isolation of a further new pyrone-substituted flavone, hosloppin [**1**].

The finely powdered leaves of *H. opposita* were extracted with MeOH. The concentrated MeOH extract, upon repeated cc and crystallization, yielded four known pentacyclic triterpenoids, 2-*epi*-tormentic acid, jacarandic acid (5) [syn. euscaphic (6) or acuminatic acid (7)], and a mixture of ursolic and oleanolic acids, together with three flavonoids, hosloppin [**1**], hoslundin [**2**], and 5-*O*-methylhoslundin [**3**]. Compound **1** was isolated and characterized for the first time.

Hosloppin [**1**], $C_{22}H_{16}O_7$, mp 230° (dec) exhibited bands in its ir spectrum consistent with the presence of hydroxyl (ν max 3200 cm^{-1}) and conjugated carbonyl (ν max 1654, 1647 cm^{-1}) groups. Color tests with $FeCl_3$ (green) and magnesium/concentrated HCl (pink) together with the uv spectral data (see Experimental), and the observation of a ^{1}H-nmr deshielded hydroxyl proton at δ 11.0, as well as a characteristic flavone H-3 signal (δ 6.90), indicated that hosloppin is a 5-hydroxyflavone. Compound **1** also exhibited ^{1}H-nmr resonances at δ 2.35 (s, Me), 3.88 (s, OMe), 7.58 (3H, m), and 8.20 (2H, m). The last two resonances arise from an unsubstituted ring B of a flavone. Fragment ions at *m/z* 102 and 105 in the ms of **1** supported the presence of an unsubstituted ring B (8). The ^{1}H- and ^{13}C-nmr spectra (Table 1) of hosloppin [**1**] were similar to those of hoslundin [**2**] isolated from the same plant (3). The only difference was the replacement in the spectrum of **1** of one methoxyl by a chelated hydroxyl group at δ 8.64. The ^{13}C-nmr spectrum of **1** was almost superimposable with that of 5-*O*-methylhoslundin [**3**]. Support for structure **1** was obtained from chemical correlation, as methylation of **1** with CH_2N_2



1 $R^1=R^2=H$
2 $R^1=Me$, $R^2=H$
3 $R^1=R^2=Me$

TABLE 1. ^{13}C-Nmr Spectral Data of Hosloppin [**1**], Hoslundin [**2**], and 5-*O*-Methylhoslundin [**3**] Recorded at 50.13 MHz.[a]

Carbon	Compound		
	1[b]	**2**[c]	**3**[c]
2	163.6	163.9	161.0
3	105.5	106.0	108.8
4	182.1	182.3	176.7
5	157.5	158.2	158.7
6	111.0	103.7	113.0
7	163.5	163.9	162.3
8	90.5	90.3	95.9
9	158.9	159.4	159.6
10	112.0	105.7	112.4
1′	130.6	131.1	131.3
2′,6′	126.3	126.3	125.9
3′,5′	128.9	129.1	128.9
4′	131.9	131.9	131.3
2″	148.2	158.1	158.4
3″	158.8	145.1	144.9
4″	182.1	173.3	173.6
5″	117.9	121.3	122.0
6″	153.6	153.6	153.2
Me	14.0	14.7	14.7
MeO-7	56.2	56.3	56.3
MeO-3″	—	60.0	59.9
MeO-5	—	—	62.3

[a]Assignments are based on chemical shifts rules and multiplicities on DEPT spectra.
[b]Measured in DMSO-d_6.
[c]Measured in $CDCl_3$.

readily gave **3**. Thus, hosloppin was assigned structure **1**.

A special feature of the *H. opposita* flavonoids is the incorporation of the pyrone unit. This C-6-affixed pyrone substituent is attached either via a 6,6″-linkage (oppositin) or a 6,5″-linkage (hoslundin, 5-*O*-methylhoslundin, and hosloppin [**1**]).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps were determined on a Kofler hot-stage apparatus and are uncorrected. Eims were obtained at 70 ev by direct inlet. Uv spectra were recorded with a Beckman spectrophotometer and ir spectra on a Perkin-Elmer instrument. Nmr spectra were run on a Bruker WP200SY spectrometer in $CDCl_3$ or DMSO-d_6 solutions unless otherwise stated (25°), at 200.13 MHz for ^{1}H (shifts relative to $CDCl_3$ or DMSO-d_6 at δ_H 7.25 and 2.5, respectively) and at 50.32 MHz for ^{13}C (shifts relative to $CDCl_3$ and DMSO-d_6 at δ_C 77.0 and 39.5). Tlc of compounds was conducted on Merck Si gel 60 F_{254}, and spots were visualized in uv light (254 or 366 nm).

PLANT MATERIAL.—The leaves of *H. opposita* were collected from Yaoundé, Central Province, Cameroon in February 1993 by Mr. A. Mizili. The identity of the plant material was confirmed at the Cameroon National Herbarium, Yaoundé, where a voucher specimen (No. 9878) has been deposited.

EXTRACTION AND ISOLATION.—The powdered, sun-dried leaves of *H. opposita* (4 kg) were extracted exhaustively with MeOH (10 liters) and the solution was concentrated under reduced pressure to give a dark green residue (350 g). Part of this residue (200 g) was chromatographed on Si gel (1 kg) packed in hexane. Gradient elution was effected with hexane, hexane/EtOAc, EtOAc, EtOAc/MeOH, and MeOH. A total of 328 fractions (500 ml each) were collected and combined on the basis of tlc comparison with an appropriate solvent system. Fractions 160–188 eluted with hexane-EtOAc (30:70) were combined to give 3 g of a mixture of three compounds as shown by tlc. This mixture was dissolved in a hot EtOAc/hexane mixture. The solution, upon cooling, gave a yellow powdered solid (145 mg) which displayed one spot on tlc for hosloppin [**1**].

Hosloppin [**1**].—Mp 230° (dec); uv λ max (MeOH) (log ε) 272 (4.22), 305 (4.01) nm; λ max (MeOH+$AlCl_3$) 280, 328, 380 nm; ir ν max (KBr) 3200 (OH), 1655 and 1650 (conjugated CO), 1610, 1584, 1570, 1560, 1540, 1500, 1490, 1450, 1440, 1350, 1230, 1200, 1170, 1130, 1120 cm^{-1}; ^{1}H nmr (200.13 MHz, DMSO-d_6) δ 11.00 (1H, br s, D_2O exchangeable, OH-5), 8.64 (1H, br s, D_2O exchangeable, OH-3″), 8.20 (2H, m, H-2′ and H-6′), 7.92 (1H, s, H-6″), 7.58 (3H, m, H-3′, H-4′, and H-5′), 6.90 (1H, s, H-3), 7.00 (1H, s, H-8), 3.88 (3H, s, OMe), 2.35 (3H, s, Me); ^{13}C-nmr, see Table 1; eims *m/z* 393 $[M+1]^+$ (18), 392 $[M]^+$ (73), 349 (15), 322 (18), 321 (90), 294 (21), 293 (100), 291 (16), 279 (14), 278 (30), 265 (13), 263 (18), 176 (14), 163 (12), 129 (11), 105 (20), 103 (12), 102 (14), 79 (13), 77 (32), 76 (12), 75 (10), 69 (26); *anal.* found C 67.25, H 4.00, $C_{22}H_{16}O_7$ requires C 67.33, H 4.11.

Methylation of hosloppin [**1**].—CH_2N_2 in Et_2O was added to a solution of **1** (20 mg) in MeOH (4 ml) at room temperature. After 30 min the solvent was evaporated to give 5-*O*-methylhoslundin [**3**] (19 mg), mp 249–250° [lit. (3) mp 249–251°].

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LITERATURE CITED

1. O.A. Onayade, L. Ntezurubanza, J.J.C. Scheffer, and A.B. Svendsen, "37th Annual Congress on Medicinal Plant Research," Braunschweig, Germany, Abstract P-81, September 5–9, 1989.
2. H. Achenbach, R. Waibel, M.H.H. Nkunya, and H. Weenen, *Phytochemistry,* **31**, 3781 (1992).
3. B.T. Ngadjui, J.F. Ayafor, B.L. Sondengam, J.D. Connolly, and D.S. Rycroft, *Tetrahedron,* **47**, 3555 (1991).
4. B.T. Ngadjui, J.F. Ayafor, B.L. Sondengam, J.D. Connolly, D.S. Rycroft, and F. Tillequin, *Phytochemistry,* **32**, 1313 (1993).
5. M. Ogura, G.A. Cordell, and N.R. Farnsworth, *Lloydia,* **40**, 157 (1977).
6. K. Takahashi, S. Kawaguchi, K.I. Nichimura, K. Kubota, Y. Tanabe, and M. Takani, *Chem. Pharm. Bull.,* **22**, 2650 (1974).
7. R.S. Chandel and R.P. Rastogi, *Ind. J. Chem.,* **15B**, 914 (1977).
8. T.J. Mabry and K.R. Markham, in: "The Flavonoids." Ed. by J.B. Harborne, T.J. Mabry, and H. Mabry, Chapman and Hall, London, 1975, p. 79.

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