Journal of Natural Products
Vol. 50, No. 3, pp. 357-359, May-Jun 1987

A NEW METHOXYLATED β-HYDROXYCHALCONE FROM *POLYGONUM NEPALENSE*[1]

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ABSTRACT.—Further examination (1) of *Polygonum nepalense* has led to the isolation of a new heptamethoxy-1,3-diketo compound [**1**] along with three known flavonoid glycosides, identified as quercetin-3-*O*-rhamnobioside, hyperoside, and luteolin-6-*C*-glucoside, and the glucoside of β-sitosterol. Structures were identified by ^{13}C-nmr and other spectroscopic methods.

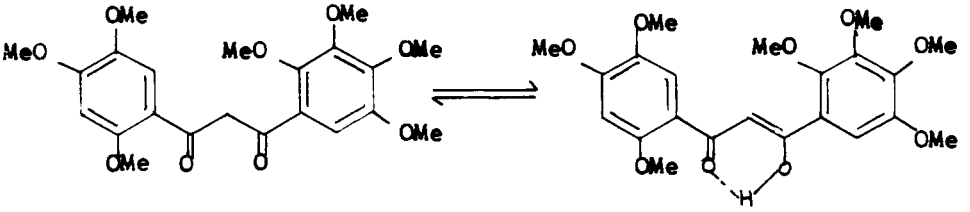
The alcoholic extract of *Polygonum nepalense* Meissn. (Polygonaceae) was fractionated into C_6H_{14} and $CHCl_3$ soluble parts. The viscous, hexane soluble material on chromatography over neutral alumina gave a yellow, viscous compound [**1**], $C_{22}H_{26}O_9$ (M^+ 434). An orange color was developed on spraying the tlc plate with 10% H_2SO_4 solution. Ir bands at 3450 and 1625 cm^{-1} indicated the tautomeric form of a β-diketone, while bands at 1580 and 1495 cm^{-1} revealed the aromatic nature of the compound. Uv absorption at 365, 310, and 262 nm indicated compound **1** to be a dibenzoyl methane. A bathochromic shift of 65 and 54 nm with $AlCl_3$ inferred the tautomeric form of compound **1**, which was further confirmed by the study of its ^{1}H-nmr spectrum. The ^{1}H-nmr spectrum in $CDCl_3$ exhibited methoxy, *trans*-olefinic, and the aromatic protons, existing in solution as an equilibrium mixture of tautomeric forms (2-4).

The ^{1}H-nmr signals at δ 4.26 (s, 0.26, -CH_2-) and δ 6.91 (s, 0.74, HC=), integrating for less than the required number of protons, were assigned to the diketonic methylene and olefinic protons in an enolic form, respectively, agreeing with the values reported for diketo chalcones (2). The existence of a bonded hydroxyl proton signal at δ 14.63 (broad hump 0.5, -OH-), which disappeared on D_2O shake, was also inconsistent with the existing ketoenolic form in compound **1** (5-7). The singlets for seven methoxyl groups appeared between δ 3.83 to δ 3.93, and the singlets at δ 6.29, δ 7.95, and δ 8.00 for one proton each were attributed to C-5′, C-2′, and C-6″ aromatic protons, respectively. ^{13}C-nmr also confirmed the tautomeric nature of compound **1**, a triplet and a doublet at 29.65 ppm and 138.10 ppm were observed for C-2 in the SFORD spectrum. A literature survey of chalcones (8,9) confirmed the positions of the other peaks.

The eims also suggested the existence of a dibenzoyl methane system in compound **1** (10). The fission of the molecule adjacent to the carbonyl group resulted in the formation of four prominent ions at *m/z* 239, 209, 195, and 167, representing explainable fragments of the rings with two integrating carbons. Compound **1** gave a mass fragment (M^+-H-31, *m/z* 402) as a base peak, which is characteristic for 2-methoxy chalcones and *ortho* methoxy dibenzoyl methanes (11).

Compound **1** was refluxed with 2,3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ)/dioxan to form the cyclized product **2**, $C_{22}H_{26}O_9$ (M^+ 434); **2** was also obtained by acid (10% H_2SO_4 and 10% HOAc, 1:1) treatment of compound **1**. The ^{1}H-nmr spectrum of compound **2** showed characteristic signals of the flavanone nucleus; the occurrence of an ABX system centered at δ 2.74, δ 2.97, and δ 5.72 revealed for H-2 and H-3 together with signals for seven methoxyl functions from δ 3.86 to δ 3.98, while the C-6 proton singlet appeared at δ 6.38, the singlet at δ 6.81 was assigned to C-

[1]CDRI Communication No. 3948



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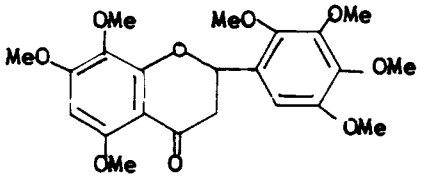

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6′ proton. RDA fragmentation in the eims suggested the presence of three methoxys in ring-A and four in ring-B with formation of ions at *m/z* 210 and 224. The appearance of singlets of varying intensity at δ 4.26 and δ 6.91 is a recurrent feature of the ^{1}H-nmr spectra of dibenzoyl methanes lacking a chelated hydroxyl (12).

The *n*-BuOH fraction of the alcoholic extractive of the plant on chromatography yielded a number of glycosidic compounds. Their identifications were suggested by color reactions as quercetin-3-*O*-rhamnobioside, quercetin-3-*O*-β-D-galactoside, and luteolin-6-*C*-glucoside along with β-sitosterol-β-D-glucoside. These compounds were characterized by their ir, uv, nmr (^{1}H, ^{13}C), and fdms of partially and fully hydrolyzed products.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Eims were recorded on JEOL JMS D300 at 70 eV; ir in KBr and $CHCl_3$ on 157 Perkin-Elmer; uv in MeOH on Hitachi 320 spectrophotometer; nmr spectra were measured on 400 MHz (Bruker), 90 MHz (Perkin-Elmer R-32) 60 MHz (EM-360), and 80 MHz (CFT-20) spectrometers in $CDCl_3$, with TMS as an internal standard. Tlc and plc were carried out on Si gel. The spots were visualized by spraying with 1% ceric sulfate in 2 N H_2SO_4 and by uv light.

PLANT MATERIAL.—*P. nepalense* syn. *P. alatum* Ham ex D. Don var. *nepalense* (Meissn) Hook F., was collected in October 1983, from Mussoorie (U.P.) and identified by Dr. B.S. Aswal, Botany Division, CDRI, Lucknow. A voucher specimen is deposited in the Medicinal Plant Herbarium of the Central Drug Research Institute, Aswal, 11228, CDRI.

EXTRACTION AND CHROMATOGRAPHY.—Dry, powdered, whole plant material (6 kg) was extracted with 95% EtOH (4×10 liters) at 40-50° under reduced pressure. The concentrated EtOH extract (580 g) was subsequently extracted with hexane, $CHCl_3$, and *n*-BuOH. The concentrated hexane-soluble residue was chromatographed over neutral Al_2O_3, which yielded compound **1** on repeated column chromatography (C_6H_{14}-$CHCl_3$, 1:1) and preparative tlc ($CHCl_3$-EtOAc, 19:1). The *n*-BuOH extract was repeatedly chromatographed over Si gel to yield a mixture of the compounds quercetin-3-*O*-rhamnobioside, quercetin-3-*O*-galactoside, and luteolin-6-*C*-glucoside which were further separated by chromatography over polyamide with EtOAc (saturated with H_2O/MeOH in sequence of increasing polarity as eluant). This resulted in the elution of pure quercetin-3-*O*-galactoside while quercetin-3-*O*-rhamnobioside was further purified by chromatography in gradient elution with Me_2CO-MeOH (8:2).

3′,4′,6′,2″,3″,4″,5″-HEPTAMETHOXY-1,3-DIKETO CHALCONE [**1**].—Obtained as a yellow viscous mass (80 mg); ir ν max 3450 (OH), 2950, 1730 (>C=O), 1625 (C(OH)=CH-C=O), 1580, 1495 (aromatic), 1325, 1290, 1140, 1110, 1080, 1020, 1000, 940, 920, 840, 760 cm^{-1}; uv λ max (log ε) 365 (2.72), 310 (2.68), 262 (2.63) nm; eims *m/z* (rel. int.) 434 (M^+, 9.6%), 433 (M^+-H, 36.73%), 402 (M^+-H-31, 100%), 386 (15.17%), 224 (M^+-210), 209, 195, 167; ^{1}H nmr δ (ppm) 4.26 (0.26, s, H-2, O=C-CH_2-C=O), 3.89 (12H, s, 4×-OCH_3), 3.93 (9H, s, 3×-OCH_3), 6.29 (1H, s, H-5′), 6.91 (0.74, s, C=O-C*H*=C-(OH)), 7.95 (1H, s, H-2′), 8.0 (1H, s, H-6″), 14.63 (0.5, br, C=O-CH=C-(OH)); ^{13}C

nmr (ppm) 123.7 (1′, s), 105.54* (2′, d), 149.71 (3′, s), 162.67 (4′, s), 96.68 (5′, d), 160.07 (6′, s), 193 (1, s, C=O), 29.65 (2, t), 138.10 (C-2 of enolic form, d), 123.7 (1″, s), 160.07 (2″, s), 126.57 (3″, d), 162.67 (4″, s), 149.71 (5″, s), 126.57* (6″, d), 54.39 (3′-OMe), 56.39 (4′-OMe), 61.73 (6′-OMe), 61.81 (2″-OMe), 59.39 (3″-OMe), 56.62 (4″-OMe), 59.39 (5″-OMe). (* values are interchangeable).

2′,3′,4′,5′,5,7,8-HEPTAMETHOXY FLAVANONE [**2**].—Compound **1** (15 mg) was cyclized with DDQ (7.3 mg), in the presence of dry dioxan (0.75 ml), by refluxing at 100° for 12 h in anhydrous conditions. The reaction mixture was cooled, and the precipitate was filtered. The filtrate was concentrated and extracted with $CHCl_3$, washed 3 to 4 times with H_2O, and dried over anhydrous Na_2SO_4. The concentrate was chromatographed and purified by plc to obtain compound **2** (7 mg) which could not be crystallized to a sharp melting product; ir ν max 1680 (C=O), 1610, 1590, 1495, 1460, 1420 (aromatic), 1260 (C-O-C), 1210, 1100, 1070, 860, 760, 705 cm^{-1}; uv λ max 320, 275, 230 nm; eims *m/z* 434 (M^+), 433 (M^+-H, 14.4%), 402 (M^+-H-OCH_3, 25.6%), 224, 210; ^1H nmr δ (ppm) 2.74 (1H, dd, J=4, 17 Hz, H-3), 2.97 (1H, dd, J=10, 17 Hz, H-3), 3.86, 3.87 (6H, each s), 3.89 (6H, 2×-OCH_3), 3.92, 3.96, 3.98 (9H, each s), 5.72 (1H, dd, J=5, 10 Hz, H-2), 6.38 (1H, s, H-6), 6.81 (1H, s, H-6′).

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Received 22 August 1986