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Benzofuran glycosides from *Psoralea plicata* seeds[1]

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Abstract

Three new benzofuran glycosides were isolated from the *N*-butanol soluble fraction of *Psoralea plicata* seeds, together with psoralic acid (6←1)-*O*-*β*-D-glucopyranoside (*E*-form), previously isolated from the aerial parts of the same plant. The structures have been determined by different spectroscopic measurements.

Keywords: Psoralea plicata; Leguminosae; Benzofuran glycosides

1. Introduction

In a previous publication (Hamed et al., 1997), we described the isolation of 16 different compounds from the aerial parts of *Psoralea plicata* Del. (=*Cullen plicatum* Delile C.H. Stirt) which is known in arabic as "Marmid" and is widely distributed in the Allaqi area south–east of Aswan (Springuel, 1994).

Now, we wish to report on the isolation and structure elucidation of a group of benzofuran glycosides from the *N*-butanol soluble fraction of the seed extract.

2. Results and discussion

A methanol extract of the dried seeds of *P. plicata* was processed as mentioned in the experimental section. The *N*-butanol soluble fraction (13 g), was subjected to ODS column chromatography, where three fractions A, B and C were obtained. Fractions B and C were separately acetylated and the acetylated fraction B was subjected to flash silica column chromatography, eluted with hexane–acetone (3:2) to give compounds **1** and **2**. Similarly acetylated fraction C treated in the same manner to give compounds **3** and **4**.

Compound **1** acetate, showed its $[M+1]^+$ at m/z 627 in the FAB mass spectrum, consistent with $C_{27}H_{32}O_{17}$. Its ^{1}H NMR spectrum (Table 1) displayed the presence of two furan protons at δ 7.55 (1H, d, $J=2.2$ Hz) and δ 6.90 (1H, dd, $J=0.8$ and 2.2 Hz), also there are two *ortho*-coupled aromatic protons at δ 7.14 (1H, d, $J=8.4$ Hz), and δ 7.24 (1H, d, $J=8.4$ Hz). The spectrum showed signals for an ethyl ester represented by a methyl group triplet at δ 0.89 (3H, t, $J=7.3$ Hz), and a typical AB quartet for methylene group at δ 4.05 (2H, q, $J=7.2$ Hz), in addition to signals for two aliphatic methylene groups at 3.03 (2H, t, $J=6.6$ Hz) and 2.61 (2H, t, $J=6.6$ Hz).

The ^{1}H NMR and ^{13}C NMR spectra showed an anomeric proton signal at δ 5.13 (1H, d, $J=9.7$ Hz) and its carbon at δ 99.68. The chemical shift and J value of the anomeric proton indicated *β*-linkage with carbon at δ 147.20.

Acid hydrolysis of compound **1** acetate with 5% HCl–MeOH, gave glucose and isocorylifonol (Lin & Kuo, 1992). So, we concluded that compound **1** was a new glycoside with a known aglycone, which is isolated from natural sources for the first time and given the structure isocorylifonol (1→4) *O*-*β*-D-glucopyranoside.

The ^{1}H NMR spectrum of compound **2** showed a great similarity to that of compound **1**, except for the benzofuran signals, which displayed slight changes where, the doublets of the two *ortho*-coupled aromatic protons in **1**, have been changed into two singlets for *p*-oriented aromatic protons in **2** at δ 7.25 and 7.01; other signals are more or less similar in the two compounds Table 1. This observation suggested a corylifonol glycoside. Acid hydrolysis as previously mentioned, gave corylifonol and glucose.

From the above mentioned data, compound **2** was suggested to be corylifonol (1→6)-*O*-*β*-D-gluco-

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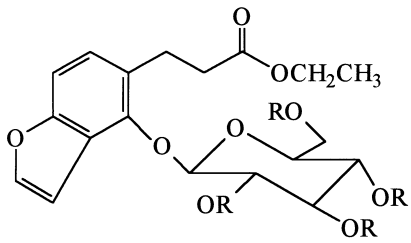

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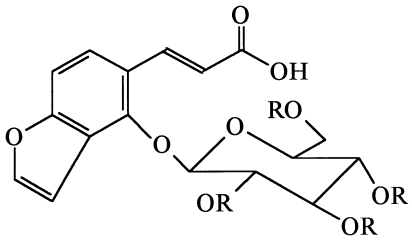

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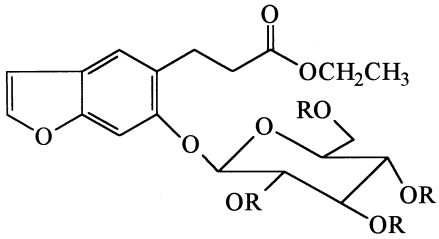

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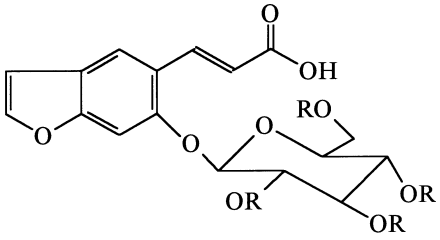

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R= Ac

Table 1
^{1}H NMR spectral data for the isolated benzofuran glycosides **1**–**4** (400 MHz, $CDCl_3$)

	1	**2**	**3**	**4**
Aglycone moieties				
C-2	7.55(1H, d, J=2.2 Hz)	7.54 (1H, d, J=2.2 Hz)	7.57 (1H, d, J=2.2 Hz)	7.60 (1H, d, J=2.2 Hz)
C-3	6.90(1H, dd, J=0.8, 2.2 Hz)	6.66(1H, dd, J=0.8, 2.2 Hz)	6.96(1H, dd, J=0.8, 2.2 Hz)	6.65(1H, dd, J=0.8, 2.2 Hz)
C-4	–	7.37(1H, s)	–	7.79(1H, s)
C-5	–	–	–	–
C-6	7.24(1H, d, J=8.4 Hz)	–	7.56(1H, d, J=8.4 Hz)	–
C-7	7.14(1H, d, J=8.4 Hz)	7.26(1H, s)	7.31(1H, d, J=8.4 Hz)	7.37(1H, s)
C-4a	–	–	–	–
C-7a	–	–	–	–
C-1′	3.03(2H, t, J=6.6 Hz)	2.96(2H, t, J=6.6 Hz)	8.21(1H, d, J=16.1 Hz)	8.04(1H,d, J=16.1 Hz)
C-2′	2.61(2H, t, J=6.6 Hz)	2.63(2H, t, J=6.6 Hz)	6.41(1H, d, J=16.1 Hz)	6.40(1H,d, J=16.1 Hz)
C-3′	–	–	–	–
C-4′	4.05(2H, q, J=7.2 Hz)	4.05(2H, q, J=7.2 Hz)		
C-5′	0.89(3H, t, J=7.3 Hz)	0.89(3H, t, J=7.3 Hz)		
CH_3CO	2.14,2.09,2.05,2.02(s)	2.13,2.09,2.04,2.03(s)	2.17,2.11,2.06,2.05(s)	2.17,2.13,2.05,2.03(s)
Glucosyl moieties				
1″	5.13(1H, d, J=7.9 Hz)	5.10(1H, d, J=7.6 Hz)	5.07(1H, d, J=7.8 Hz)	5.08(1H, d, J=7.8 Hz)
2″	5.37(1H, t, J=9.4 Hz)	5.38(1H, t, J=9.4 Hz)	5.44(1H, t, J=9.4 Hz)	5.42(1H, t, J=9.4 Hz)
3″	5.32(1H, t, J=9.4 Hz)	5.28(1H, t, J=9.4 Hz)	5.34(1H, t, J=9.4 Hz)	5.30(1H, t, J=9.4 Hz)
4″	5.16(1H, t, J=9.4 Hz)	5.16(1H, t, J=9.4 Hz)	5.20(1H, t, J=9.4 Hz)	5.18(1H, t, J=9.4 Hz)
5″	3.57(1H, m)	3.59(1H, m)	3.68(1H, m)	3.93(1H, m)
6″	4.12(1H, dd, J=2.4, 12 Hz)	4.13(1H, dd, J=2.4, 12 Hz)	4.06(1H, dd, J=1.1, 12 Hz)	4.26(2H, dd, J=2.6, 12 Hz)
	4.21(1H, dd, J=2.4, 12 Hz)	4.30(1H, dd, J=2.4, 12 Hz)	4.25(1H, dd, J=1.1, 12 Hz)	

Multiplicity was detected by DEPT experiment.

pyranoside, isolated for the first time as a natural product and its aglycone was isolated previously from *Psoralea corylifolia* (Lin & Kuo, 1992).

The ^{1}HNMR spectrum of compound **3** was similar in the major part to compound **1** Table 1, with a characteristic absence of the signals for the ethyl ester group and significant changes of the signals for the two aliphatic methylene groups (two triplets at δ 3.03 and 2.61), into a cinnamic acid residue (two *trans*-coupled olefinic protons) at δ 8.21 and 6.41 (each 1H, d, $J=16.10$ Hz). The mass spectrum of compound **3** acetate, showed its $[M]^+$ at m/z 534 in the FAB mass spectrum, consistent with $C_{25}H_{26}O_{13}$, which is less than compound **1** with mass unit equivalent to $C_2H_5+H_2$. The CH–COSY spectrum of compound **3**, revealed a cross peak between a proton at δ 5.07 and carbon at δ 100.94 (HMQC) and a cross peak between a proton at δ 6.96 and carbon at δ 157.65, which in turn showed a cross peak with proton at δ 7.56, which exhibited a cross peak with carbons at δ 140.90 and 148.81.

The ^{1}HNMR and ^{13}CNMR spectra of compound **3** (Tables 1–2), displayed one anomeric proton signal at δ 5.07 (1H, d, $J=7.8$ Hz) and its carbon at δ 100.94 showed a cross peak with carbon at 148.81 indicating β- linkage of the sugar at C-4. The ^{13}C NMR spectrum showed four signals for acetate groups, four methines and one methylene for a sugar molecule (DEPT experiment). Acid hydrolysis of compound **3** gave glucose and a benzofuran compound closely related to psoralic acid (Stoll, Pereira, & Renz, 1950). So, the isolated compound was assumed to be a new glycoside named isopsoralic acid (1→4)-*O*-β-D-glucopyranoside, a new natural product isolated from natural sources for the first time.

The ^{1}H NMR and ^{13}C NMR spectra of compound **4**, were very close to compound **3**, except for the distributin of the aromatic proton signals as shown in Table 1. Comparative matching of the data obtained for this compound, as well as examination of its hydrolytic products, revealed that it should be psoralic acid (1→6)-*O*-β-D-glucopyranoside (*E*-form), we previously reported from the aerial parts of the same plant, and its aglycone (psoralic acid *E*-form) was reported from *Coronilla glauca* (Stoll et al., 1950).

3. Experimental

Optical rotations were measured on a JASCO-360 digital polarimeter; UV spectra were obtained on a Hitachi 200-10 spectrophotometer; IR spectra were taken on JASCO IR-A-2 spectrophotometer; ^{1}H and ^{13}C NMR spectra were taken on Bruker AM-400 and AM-500; MS spectra were obtained on Hitachi RMU-7M spectrometer.

Table 2
^{13}C NMR spectral data for the isolated benzofuran glycosides **1**–**4** (100 MHz, $CDCl_3$)

	1	2	3	4
Aglycone moieties				
C-2	144.63(d)	144.95(d)	145.22(d)	146.14(d)
C-3	100.1(d)	106.26(d)	105.23(d)	106.57(d)
C-4	147.20(s)	121.65(d)	148.81(s)	120.2 0(d)
C-5	120.39(s)	121.65(s)	121.79(s)	121.40(s)
C-6	126.17(d)	155.36(s)	123.36(d)	153.51(s)
C-7	108.29(d)	106.26(d)	109.38(d)	101.83(d)
C-4a	120.30(s)	126.16(s)	121.17(s)	123.57(s)
C-7a	157.65(s)	157.65(s)	157.65(s)	156.54(s)
C-1′	35.17(t)	34.42(t)	140.90(d)	141.37(d)
C-2′	30.66(t)	29.70(t)	117.61(d)	117.52(d)
C-3′	173.12(s)	173.12(s)	171.54(s)	171.54(s)
C-4′	64.86(t)	64.86(t)	–	–
C-5′	19.11(q)	21.69(q)	–	–
4CH_3CO	20.59(q)	20.72(q)	20.56(q)	20.63(q)
C=O	169.24, 169.36, 170.31, 170.49(s)	169.31, 169.45, 170.32, 170.51(s)	169.33, 169.49, 170.24, 170.50(s)	169.40, 169.59, 170.27, 170.62(s)
Sugar moieties				
1″	99.68(d)	99.04(d)	100.94(d)	100.38(d)
2″	68.34(d)	68.53(d)	68.29(d)	68.4(d)
3″	71.69(d)	71.90(d)	71.58(d)	71.58(d)
4″	72.01(d)	72.20(d)	72.88(d)	72.7(d)
5″	72.98(d)	72.87(d)	72.08(d)	72.3(d)
6″	62.0(t)	62.15(t)	61.85(d)	62.0(t)

Multiplicity was detected by DEPT experiment.

3.1. Extraction and isolation of the constituents

The air-dried seeds of *P. plicata* (1 kg) were powdered, defatted with hexane at room temperature and extracted with MeOH (75% by maceration). The alcoholic extract was concd. under red. pres. to a syrupy consistency (73 g). The solvent free residue (25 g) was mixed with 100 ml water, 50 ml MeOH, transferred to a separatory funnel and partitioned between $CHCl_3$ and *N*-BuOH. Each fraction was dried over anhydrous sodium sulphate and concd. under red. pres. ($CHCl_3$ residue, 10 g; *N*-BuOH residue, 13 g).

3.2. Separation of the N-butanol components

The *N*-BuOH fraction (13 g) was subjected to ODS column chromatography eluted with MeOH–H_2O (8:2) to give three fractions **A**, **B** and **C** (9, 2.5 and 1 g respectively). Fractions **B** and **C** (100 mg each was separately acetylated with Ac_2O in dry pyridine and processed in the usual manner. The acetylated products were separated on flash silica CC eluted with hexane–Me_2CO (3:2), where fraction **B** gave compounds **1** (20 mg) and **2** (15 mg). Similarly fraction **C** gave compounds **3** (30 mg) and **4** (17 mg).

Compound **1**: isocorylifonol (4←1)-*O*-*β*-D-glucopyranoside acetate. Colourless gum $[\alpha]_D$ −9.99 ($c=0.006$, $CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 1730 (ester), 1725 (C═O), 2900 (CH stretching), 1680 (furan), 1620 (C═C). Positive FAB–MS m/z (rel. int.): 627 $[M–H]^+$ ($C_{27}H_{32}O_{17}$)(27), 392 [M-4 acetate]$^+$ (60), 347 [M-4 acetate-OC_2H_5]$^+$ (25); UV $\lambda_{max}^{CHCl_3}$ nm: 206, 244, 250, 290. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$): Tables 1 and 2.

Compound **2**: corylifonol (6←1)-*O*-*β*-D-glucopyranoside acetate. Colourless gum, $[\alpha]_D$ −3.33 ($c=0.006$, $CHCl_3$); IR, ν_{max}^{KBr} cm^{-1}: 1730 (ester), 1725 (C═O), 2900 (CH stretching), 1680 (furan), 1620 (C═C). Positive FAB–MS m/z (rel. int.): 627 $[M–H]^+$ ($C_{27}H_{32}O_{17}$) (27), 392 [M-4 acetate]$^+$ (60), 347 [M-4 acetate-OCH_2CH_3]$^+$ (25); UV $\lambda_{max}^{CHCl_3}$ nm: 206, 244, 250, 290. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$): Tables 1 and 2.

Compound **3**: isopsoralic acid-(4←1)-*O*-*β*-D-glucopyranoside acetate. Colourless gum, $[\alpha]_D$ −70 ($c=0.02$ $CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 1725 (C═O), 2900 (CH stretching), 1680 (furan), 1620 (C═C). Positive FAB–MS m/z (rel. Int.): 534 $[M]^+$ ($C_{25}H_{26}O_{13}$) (70), 368 [M+2H-4 acetate]$^+$ (65), 186 $[M–C_{11}H_6O_3]^+$ (15), 169 $[M–C_{11}H_7O_4]^+$ (75). UV $\lambda_{max}^{CHCl_3}$ nm: 255, 300. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}CNMR (100 MHz, $CDCl_3$): Tables 1 and 2.

Compound **4**: psoralic acid-(6←1)-*O*-*β*-D-glucopyranoside acetate. Colourless gum, $[\alpha]_D$ −50 ($c=0.02$ $CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1725 (C═O), 2900 (CH stretching), 1680 (furan), 1620 (C═C). Positive FAB–MS m/z (rel. int.): 534 $[M]^+$ ($C_{25}H_{26}O_{13}$) (35), 368 [M+2H-4 acetate]$^+$ (38), 186 $[M–C_{11}H_6O_3]^+$ (15), 169 $[M–C_{11}H_7O_4]^+$ (75); UV $\lambda_{max}^{CHCl_3}$ nm: 255, 300. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$): Tables 1 and 2.

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