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METHYLATED CHALCONES FROM *BIDENS TORTA*

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Key Word Index—*Bidens torta*, Compositae, chalcones, okanin 3,4,3',4'-tetramethyl ether, okanin 3,4,3'-trimethyl ether 4'-glucoside, okanin 3,4-dimethyl ether 4'-glucoside, okanin 4-methyl ether 4'-glucoside, okanin 4-methyl ether 4'-glucoside monoacetate

Abstract—Four new natural products, all methylated chalcones, including an acetylated glycoside, were isolated from *Bidens torta* Their structures were determined by spectroscopic methods as okanin 3,4,3',4'-tetramethyl ether, okanin 3,4,3'-trimethyl ether 4'-glucoside, okanin 4-methyl ether 4'-glucoside and okanin 4-methyl ether 4'-glucoside monoacetate Okanin 3,4-dimethyl ether 4'-glucoside was also isolated

INTRODUCTION

Members of the subtribe Coreopsidinae (Compositae) are characterized by the presence of resorcinol-based anthochlor pigments [1] Species of *Bidens* typically contain the chalcones butein, okanin and lanceolin and their 4'-glycosides There are a few reports of B-ring methylated chalcones in the genus *B ferulaefolia* contains two methylated chalcones tentatively identified as 2',3'-dihydroxy-4,4'-dimethoxychalcone and 2'-hydroxy-4,4'-dimethoxychalcone [2] *B beckii* (*Megalodonta beckii*) contains butein 4-methyl ether [3] The *B pilosa* complex contains okanin 3-methyl ether 4'-glucoside and okanin 3,4-dimethyl ether 4'-glucoside [4]

In the present study, five methylated derivatives of okanin (3,4,2',3',4'-pentahydroxychalcone), including four new natural products, were isolated from *B torta* and structurally characterized

RESULTS AND DISCUSSION

Five compounds (**1**–**5**) were isolated All appeared dark under UV light and did not change with either ammonia vapours or after spraying with Naturstoffreagenz A

The UV spectrum of **1** exhibited a major absorbance in methanol at 374 nm typical of a chalcone A bathochromic shift of 42 nm after the addition of aluminium chloride and hydrochloric acid was consistent with the presence of a 2'-hydroxyl group Hydrolysis with 0 1 M hydrochloric acid yielded glucose and a chalcone aglycone The shift in the UV spectrum of the aglycone after the addition of sodium methoxide was typical of a chalcone with a substituted 4-position and a free 4'-position, suggesting that the sugar was removed from the 4'-position

The ^{1}H NMR spectrum in CD_3OD exhibited an okanin set of aromatic signals doublets for the α- and β-protons appeared at δ7 65 and 7 88, respectively, doublets for the A-ring 5'- and 6'-protons appeared at δ6 50 and 7 90, respectively, and B-ring signals appeared as a doublet at δ7 00 (H-5), a doublet at 7 40 (H-2) and a doublet at 7 33 (H-6) Two methyl singlets were present at δ3 94 and 3 87

The electron-impact mass spectrum of **1** exhibited an aglycone fragment at m/z 316 requiring two methoxyl and three hydroxyl groups The presence of a 2'-hydroxyl group, as indicated by the UV data, causes flavanone fragmentation to predominate in the mass spectrum [5] Fragments at m/z 164 and 152 were consistent with a B_1-fragment with two methoxyl groups and an A_1-fragment with two hydroxyl groups Compound **1** was identified as okanin 3,4-dimethyl ether 4'-glucoside

The UV spectrum of **2** had a maximum absorbance at 369 nm A bathochromic shift of 43 nm after the addition of aluminium chloride and hydrochloric acid confirmed the presence of a 2'-hydroxyl group The addition of sodium methoxide caused little change in the spectrum, suggesting that both the 4- and 4'-positions were substituted Hydrolysis with hydrochloric acid yielded glucose and a chalcone aglycone The addition of sodium methoxide to the aglycone solution caused the appearance of a shoulder at 410 nm consistent with a substituted 4-position and a free 4'-position The ^{1}H NMR spectrum confirmed an okanin substitution pattern In addition, three methyl singlets were present at δ3 85, 3 89 and 3 93

The electron-impact mass spectrum of **2** exhibited an aglycone fragment at m/z 330 requiring the presence of three methoxyl and two hydroxyl groups A B_1-fragment with two methoxyl groups was present at m/z 164 and an A_1-fragment with one hydroxyl group and one methoxyl group was present at m/z 166 Compound **2** was identified as okanin 3,4,3'-trimethyl ether 4'-glucoside

Compound **3** appeared to be an aglycone by chromatography Its UV spectrum in methanol exhibited a maximum absorbance at 371 nm A bathochromic shift of 39 nm after the addition of aluminium chloride and hydrochloric acid confirmed the presence of a 2'-hydroxyl group Hydrolysis with hydrochloric acid yielded glucose and a chalcone aglycone The aromatic region of the ^{1}H NMR spectrum was consistent with an okanin substitution pattern Four methyl singlets were present at δ3 82, 3 88, 3 93 and 3 95

The electron-impact mass spectrum of **3** exhibited an $[M]^+$ at m/z 344 requiring four methoxyl groups and one hydroxyl group The UV data indicated that the hydroxyl group was at the 2'-position and that there would be flavanone fragments in the mass spectrum A fragment at m/z 180 was consistent with an A_1-fragment with two methoxyl groups and a fragment at m/z 164 was consistent with a B_1-fragment with two methoxyl groups Com-

pound 3 was identified as okanin 3,4,3',4'-tetramethyl ether

The UV spectrum of 4 exhibited an absorbance maximum at 372 nm A bathochromic shift of 39 nm after the addition of aluminium chloride and hydrochloric acid indicated that there was a 2'-hydroxyl group Hydrolysis with hydrochloric acid yielded glucose and a chalcone aglycone The ^{1}H NMR spectrum was consistent with an okanin substitution pattern One methyl singlet was present at δ3 92

The electron-impact mass spectrum of 4 exhibited an aglycone fragment at m/z 302 requiring one methoxyl and four hydroxyl groups A fragment at m/z 152 was consistent with an A_1-fragment with two hydroxyl groups and a fragment at m/z 150 was consistent with a B_1-fragment with one hydroxyl and one methoxyl group Compound 4 was identified as okanin 4-methyl ether 4'-glucoside

Compound 5 had a faster migration in organic solvents than 4 The two compounds had essentially identical UV and mass spectral data Hydrolysis yielded glucose and a chalcone aglycone The ^{1}H NMR spectrum of 5 had, in addition to an okanin set of aromatic proton signals and one methyl singlet at δ3 90, an acetyl methyl singlet at δ2 06 Compound 5 was identified as okanin 4-methyl ether 4'-glucoside monoacetate

EXPERIMENTAL

Plant material Leaves of *B torta* Sherff were collected from greenhouse-grown plants The seeds were collected on 29 June 1979 at Mt Kaala, Oahu (Collection No 8629, R Ornduff)

Extraction and separation Ground air-dried leaves (30 g) of *B torta* were extracted with aq MeOH After solvent was removed under red pres the remaining syrup was redissolved in boiling H_2O and gravity-filtered through Celite The filtrate was extracted with *n*-BuOH The *n*-BuOH soluble fraction was taken to dryness and chromatographed over an LH-20 column beginning with 20% aq MeOH and gradually increasing amounts of MeOH Ten fractions were collected The first four fractions contained polyacetylenic material The remaining flavonoid-containing fractions were combined and separated further on Polyclar columns using $CHCl_3$–MeOH (3 1) Final purification on polyamide TLC using C_6H_6–MeCOEt–MeOH–H_2O (55 22 20 3) furnished okanin 3,4-dimethyl ether 4'-glucoside (1) (80 mg), okanin 3,4,3'-trimethyl 4'-glucoside (2) (150 mg), okanin 3,4,3',4'-tetramethyl ether (3) (160 mg), okanin 4-methyl ether 4'-glucoside (4) (30 mg), and okanin 4-methyl ether 4'-glucoside monoacetate (5) (30 mg) Aglycones of 1, 4 and 5 were co-chromatographed with synthetic standards

Okanin 3,4-dimethyl ether 4'-glucoside (1) ^{1}H NMR (90 MHz, CD_3OD) δ3 88 (3H, *s*, OMe), 3 92 (3H, *s*, OMe), 6 50 (1H, *d*, J = 9 Hz, H-5'), 7 00 (1H, *d*, J = 8 Hz, H-5), 7 33 (1H, *dd*, $J_{6,5}$ = 8 Hz, $J_{6\ 2}$ = 2 Hz, H-6), 7 40 (1H, *d*, J = 2 Hz, H-2), 7 65 (1H, *d*, J = 15 Hz, H-α), 7 88 (1H, *d*, J = 15 Hz, H-β), 7 90 (1H, *d*, J = 9 Hz, H-6') MS (probe) 70 eV m/z (rel int) 316 [aglycone]$^+$ (15), 152 $[A_1]^+$ (24), 164 $[B_1]^+$ (60), 149 $[B_1 - Me]^+$ UV λnm MeOH 372, 260; + NaOMe 394, + $AlCl_3$ 424, + $AlCl_3$/HCl 418

Okanin 3,4,3'-trimethyl ether 4'-glucoside (2) ^{1}H NMR (90 MHz, CD_3OD) δ3 85 (3H, *s*, OMe), 3 89 (3H, *s*, OMe), 3 93 (3H, *s*, OMe), 6 61 (1H, *d*, J = 9 Hz, H-5'), 6 95 (1H, *d*, J = 8 Hz, H-5), 7 33 (1H, *dd*, $J_{6,5}$ = 8 Hz, $J_{6\ 2}$ = 2 Hz, H-6), 7 40 (1H, *d*, J = 2 Hz, H-2), 7 65 (1H, *d*, J = 15 Hz, H-α), 7 90 (1H, *d*, J = 15 Hz, H-β), 8 00 (1H, *d*, J = 9 Hz, H-6') MS (probe) 70 eV m/z (rel int) 330 [aglycone]$^+$ (23), 166 $[A_1]^+$ (12), 164 $[B_1]^+$ (58), 149 $[B_1 - Me]^+$ (19) UV λnm MeOH 369, 256, + NaOMe 440 sh, 363, + $AlCl_3$ 422, 336, + $AlCl_3$/HCl 411, 336

Okanin 3,4,3',4'-tetramethyl ether (3) ^{1}H NMR (90 MHz, CD_3OD) δ3 82 (3H, *s*, OMe), 3 88 (3H, *s*, OMe), 3 93 (3H, *s*, OMe), 3 95 (3H, *s*, OMe), 6 70 (1H, *d*, J = 9 Hz, H-5'), 7 01 (1H, *d*, J = 8 Hz, H-5), 7 32 (1H, *dd*, $J_{6,5}$ = 8 Hz, $J_{6\ 2}$ = 2 Hz, H-6), 7 40 (1H, *d*, J = 2 Hz, H-2), 7 69 (1H, *d*, J = 15 Hz, H-α), 7 95 (1H, *d*, J = 15 Hz, H-β), 7 98 (1H, *d*, J = 9 Hz, H-6') MS (probe) 70 eV m/z (rel int) 344 $[M]^+$ (74), 180 $[A_1]^+$ (42), 164 $[B_1]^+$ (100), 149 $[B_1 - Me]^+$ (35) UV λnm MeOH 371, + NaOMe 420 sh, 344, + $AlCl_3$ 410, + $AlCl_3$/HCl 410

Okanin 4-methyl ether 4'-glucoside (4) ^{1}H NMR (90 MHz, CD_3OD) δ3 92 (3H, *s*, OMe), 6 85 (1H, *d*, J = 9 Hz, H-5'), 6 95 (1H, *d*, J = 8 Hz, H-5), 7 20 (1H, *dd*, $J_{6,5}$ = 8 Hz, $J_{6\ 2}$ = 2 Hz, H-6), 7 30 (1H, *d*, J = 2 Hz, H-2), 7 60 (1H, *d*, J = 15 Hz, H-α), 7 70 (1H, *d*, J = 9 Hz, H-6'), 7 83 (1H, *d*, J = 15 Hz, H-β) MS (probe) 70 eV m/z (rel int) 302 [aglycone]$^+$ (48), 152 $[A_1]^+$ (69), 150 $[B_1]^+$ (100), 135 $[B_1 - Me]^+$ (42) UV λnm MeOH 372, 315 sh, 262, + NaOMe 416, 348, 256, + $AlCl_3$ 424, + $AlCl_3$/HCl 411

Okanin 4-methyl ether 4'-glucoside monoacetate (5) ^{1}H NMR (90 MHz, CD_3OD) δ3 90 (3H, *s*, OMe), 6 85 (1H, *d*, J = 9 Hz, H-5'), 6 92 (1H, *d*, J = 8 Hz, H-5), 7 18 (1H, *dd*, $J_{6,5}$ = 8 Hz, $J_{6\ 2}$ = 2 Hz, H-6), 7 25 (1H, *d*, J = 2 Hz, H-2), 7 55 (1H, *d*, J = 15 Hz, H-α), 7 60 (1H, *d*, J = 9 Hz, H-6'), 7 80 (1H, *d*, J = 15 Hz, H-β) MS (probe) 70 eV m/z (rel int) 302 $[M]^+$ (17), 152 $[A_1]^+$ (45), 150 $[B_1]^+$ (68), 135 $[B_1 - Me]^+$ (29) UV λnm MeOH 370, + NaOMe 400, 336, + $AlCl_3$ 427, + $AlCl_3$/HCl 412

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