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POLYACETYLENES, TERPENOIDS AND FLAVONOIDS FROM *BUPLEURUM SPINOSUM*

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Key Word Index—*Bupleurum spinosum*; Umbelliferae; flavonoids; polyacetylenes; germacrenes; triterpenoids.

Abstract—From the aerial parts of *Bupleurum spinosum*, four new natural products have been isolated: (3*E*,5*Z*,7*Z*,9*E*)-trideca-3,5,7,9-tetraene,10(14)-trien-1-ol,*Z*-8-decene-4,6-diyn-1-ol, (*E*,*E*)-pentadeca-5,7-diene-9,11,13-triyn-2-one,tamarixetin 3-robinobioside. A series of esters of achilleol A with fatty acids has been also found.

INTRODUCTION

The genus *Bupleurum* is widely used in Chinese and Japanese traditional medicine. Nowadays, the main phytochemical studies of *Bupleurum* species are carried out on the roots, whose chemical profile is mostly constituted of saikosaponins [1, 2]. It is known that this genus also produces flavonoids, polyacetylenes and lignans [3]. In this paper, we report on the constituents of the aerial parts of *Bupleurum spinosum* L. This study is a part of our investigation into the medicinal plants of the southern Spain and northern Morocco.

RESULTS AND DISCUSSION

The leaves of *B. spinosum* were extracted successively with hexane, EtOAc and EtOH. The hexane extract was chromatographed over silica gel to yield hydrocarbon **1**, betulin, germacrenes **2** and **3**, triterpenoid **4** and polyacetylene **5**. From the EtOAc extract, the flavonoid tamarixetin (**6**) [4] precipitated. The mother liquors were chromatographed on silica gel to afford polyacetylene **7**. The EtOH extract was partitioned between BuOH and H_2O. The BuOH extract, after silica gel chromatography, furnished the flavonoid glycosides tamarixetin 3-*O*-*β*-D-galactopyranoside (**8**) [5] and **9**, as well as ribitol. **1**, **3**, **4**, **5**, **7** and **9** are new natural products.

Compound **1** gave rise to an $[M]^+$ peak at *m/z* 176, which, together with the ^1H NMR and ^{13}C NMR spectral data, were in agreement with a molecular formula $C_{13}H_{20}$. In the UV spectrum, bands at 280.4, 276.4, 269.8, 226.0 and 203.4 nm indicated the presence of conjugated double bonds. This was confirmed by IR absorption bands at 3017 and 1632 cm^{-1}. The ^{13}C NMR spectrum showed the presence of four disubstituted double bonds, besides three methylene and two methyl groups. To assign the NMR spectra, two-dimensional experiments were carried out (^1H–^1H COSY, ^1H–^{13}C HETCOR and ^1H–^{13}C COLOC). Thus, the molecule was found to be a trideca-3,5,7,9-tetraene. The configurations of the C-3/C-6 and C-7/C-8 double bonds were assigned as *Z* and those of C-3/C-4 and C-9/C-10 as *E* on the basis of the values of the NMR coupling constants and of the results for the selective irradiations of various protons. Therefore, the structure of **1** was established as (3*E*,5*Z*,7*Z*,9*E*)-trideca-3,5,7,9-tetraene.

The spectral data of compounds **2** and **3** were very similar and consistent with the structures of a germacrane-type sesquiterpenoid with **3** as the alcohol and **2** its acetate derivative. Saponification of **2** and **3** and acetylation of **3** yielded **2**. Compound **2** was identified as germacra-4(15)-5,10(14)-trien-1-yl acetate. Several diastereoisomers have been described as having this structure [6–9]. We have detected a mismatch in the assignments of the chiral centres between

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text and chemical formulae in these papers, and we have concluded that the configurations were correct in the pictures of Ref. 6. The ^{1}H NMR and ^{13}C NMR spectra of **2** were identical to those of germacra-4(15)-5,10(14)-trien-1β-yl acetate and its optical rotation ($[\alpha]_D^{25}$ −102.4°) was almost the same as the 1*R*,7*S* isomer, isolated from the brown alga *Dilophus fasciola* ($[\alpha]_D^{25}$ −106.5°C) [8]. Thus, compound **3** was (1*R*,7*S*)-germacra-4(15)-5,10(14)-trien-1-ol. Its optical rotation ($[\alpha]_D^{25}$ −134.6°) was different from the value of the product resulting from the alkaline hydrolysis of **2** described in the lit. ($[\alpha]_D^{25}$ −180.3°) [8], but very similar, in absolute value, to that of its enantiomer isolated from *Jackiella javanica* ($[\alpha]_D^{25}$ −146.3°) [7].

The IR spectrum of compound **4** showed bands of an ester group (1734 and 1243 cm^{-1}) and C=C bonds (1645, 893 and 850 cm^{-1}). The ^{1}H NMR spectrum was almost superimposable on that of achilleol A, isolated by our research group from *Achillea odorata* [10], but in **4** the double doublet corresponding to H-3 appeared at δ 4.67. This proton being geminal to an ester group. On the other hand, there was a broad singlet at δ 1.30 corresponding to a chain of methylene groups, and a triplet at δ 0.87 to a methyl group. The ^{13}C NMR spectrum confirmed the structure of achillyl A alcaneate. Saponification of **4** with KOH/MeOH gave achilleol A and a mixture of fatty acids of 12, 14 and 16 carbons. So **4** was determined to be a series of esters of achilleol A with fatty acids. It is the second time that this triterpenoid with an achillane skeleton has been found in a plant.

Compound **5** was obtained as an oil with the molecular formula $C_{10}H_{12}O$ (EIMS, $[M]^+ = m/z$ 148, and ^{1}H and ^{13}C NMR data). In its IR spectrum, the absorption bands of a hydroxyl group (3463 cm^{-1}), C≡C bonds (2331 and 2299 cm^{-1}) and a C=C bond (1666 cm^{-1}) were observed. In the ^{1}H NMR spectrum, the signals of a *cis*-disubstituted double bond appeared at δ 5.46 (1H, *dd*, J_1 = 1.7 Hz, J_2 = 10.8 Hz) and 6.08 (1H, *dq*, J_1 = 7.0 Hz, J_2 = 10.8 Hz). A triplet at δ 3.72 (2H, J = 6.1 Hz) indicated that the hydroxyl group was primary. In the ^{13}C NMR spectrum, the peaks of two substituted C≡C bonds (δ 65.67, 72.23, 78.40 and 83.92) were observed. Two-dimensional experiments (^{1}H–^{1}H COSY, ^{1}H–^{13}C HETCOR and ^{1}H–^{13}C HMBC) established the carbon skeleton for this linear polyacetylene.

Compound **7** was a yellow solid with a molecular formula $C_{15}H_{14}O$ ($[M]^+$ at m/z 210 in its mass spectrum). The IR spectrum showed bands of acetylenic groups (2234, 2205 and 2177 cm^{-1}), a carbonyl group (1708 cm^{-1}) and conjugated double bonds (1628 cm^{-1}). The UV spectrum confirmed the conjugation of the bonds with absorption maxima at 348.0, 334.4, 325.4, 312.6, 305.6, 293.8, 289.0, 279.6, 268.8, 258.8, 225.0 and 204.4 nm. The ^{1}H and ^{13}C NMR spectra revealed the presence of two *E* disubstituted C=C bonds (J = 15.2 and 15.5 Hz), two methylene groups, three C≡C bonds and two methyl groups, one adjacent to the keto function and the other joined to a triple bond. The connectivities were determined on the basis of the two-dimensional experiments (^{1}H–^{1}H COSY, ^{1}H–^{13}C HETCOR and ^{1}H–^{13}C HMBC).

Compound **9** was assigned the molecular formula $C_{28}H_{32}O_{15}$ (MS, ^{1}H and ^{13}C NMR). The IR spectrum showed bands of hydroxyl groups (3404 cm^{-1}), an α,β-unsaturated ketone (1653 cm^{-1}), and aromatic rings (1600, 1562, 1507 cm^{-1}). The ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) of the flavonoid tamarixetin (**6**), its glycosyl derivative **8** and **9** were very similar, but in **9** there was an additional unit of sugar that was identified as α-L-rhamnose. HMBC experiments permitted us to distinguish the signals of the rhamnosyl, galactosyl and aglycone moieties in **9**. On comparing the ^{13}C chemical shifts of **9** with those of **8**, it was found that C-6″ was shifted downfield by 4.9 ppm and the neighbouring C-5″ signal was shifted upfield by 2.3 ppm (Table 2). These spectral data suggested that **9** was the C-6″ α-L-rhamnosyl derivative of **8**.

EXPERIMENTAL

Extraction and isolation

Leaves were collected in June 1993 in Ketama (North of Morocco) and were identified by Professor M. Ater (Laboratoire de Biologie, Université de Tétouan-Morocco). The air-dried material (805 g) was successively extracted with hexane, EtOAc and EtOH. The hexane extract was defatted (7.6 g) and chromatographed over silica gel, eluted with hexane–Et_2O mixtures of increasing polarity (from 10:0 to 8:2) to yield 66 frs. Frs 5 to 10 afforded **1** (926 mg), fr. 28 furnished betulin (580 mg) and frs 11 to 24 (1.1 g) were subjected to repeated chromatography on silica gel eluted with hexane–Et_2O (19:1) to yield compound **2** (34 mg), **3** (222 mg), **4** (78 mg) and **5** (39 mg).

(*E*,5*Z*,7*Z*,9*E*)-Trideca-3,5,7,9-tetraene (**1**). Oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3017, 2962, 2931, 2872, 2866, 1632, 1377, 1313, 1268, 1067, 993, 953, 873, 732; UV λ_{max}^{MeOH} nm (log ε): 203.4 (3.8), 226.0 (3.2), 269.8 (4.1), 276.4 (3.9), 280.4 (4.0); EIMS (probe) 70 eV, m/z (rel. int.): 176 $[M]^+$ (47), 161 $[M-Me]^+$ (2), 147 (22), 133 (23), 119 (18), 117 (13), 106 (7), 105 (50), 92 (11), 91 (100), 79 (34), 77 (22), 67 (15), 55 (21), 41 (35); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (3H, *t*, J = 7.4 Hz, H-13), 1.02 (3H, *t*, J = 7.5 Hz, H-1), 1.43 (2H, *sext.*, J = 7.5 Hz, H-12), 2.19 (2H, *dq*, J_1 = 7.5 Hz, J_2 = 1.6 Hz, H-11), 2.22 (2H, *dquint.*, J_1 = 7.5 Hz, J_2 = 1.5 Hz, H-2), 5.46 (2H, *dtdd* J_1 = 2.6 Hz, J_2 = 7.8 Hz, J_3 = 17.7 Hz, H-3, H-10), 6.03 (1H, *ddt*, J_1 = 1.6 Hz, J_2 = 11 Hz, J_3 = 17.7 Hz, H-4), 6.09 (1H, *ddt*, J_1 = 1.6 Hz, J_2 = 11 Hz, J_3 = 17.7 Hz, H-9), 6.27 (2H, *ddd*, J_1 = 9.6 Hz, J_2 = 9.8 Hz, J_3 = 11 Hz, H-6, H-7), 6.49 (2H, *ddtt*, J_1 = Hz, J_2 = 3.3 Hz, J_3 = 9.6 Hz, J_4 = 9.8 Hz, H-5, H-8); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8 (C-13), 14.3 (C-1), 21.3 (C-2), 22.9 (C-12), 30.1 (C-11), 128.1** (C-5), 128.3 (C-9), 128.3** (C-8), 129.0 (C-4), 132.7 (C-10), 132.9* (C-7), 132.9* (C-6), 134.4 (C-3). *,** Interchangeable values.

Table 1. ^{1}H NMR spectral data for compounds **6**, **8** and **9** (DMSO-d_6, 500 MHz)

H	6	8	9
6	6.18 *d* (1.9)	6.20 *d* (2.0)	6.20 *d* (2.0)
8	6.28 *d* (1.9)	6.42 *d* (2.0)	6.42 *d* (2.0)
2′	7.75 *d* (2.0)	8.02 *d* (2.0)	8.00 *d* (1.9)
5′	6.97 *d* (8.4)	6.90 *d* (8.4)	6.90 *d* (8.4)
6′	7.70 *dd* (2.0, 8.4)	7.50 *dd* (2.0, 8.4)	7.70 *dd* (1.9, 8.4)
OCH_3	3.83 *s*	3.84 *s*	3.82 *s*
1″		5.35 *d* (7.8)	5.44 *d* (7.8)
2″		3.82 *dd* (7.8, 9.6)	3.81 *dd* (7.8, 9.6)
3″		3.56 *dd* (3.5, 9.5)	3.52 *dd* (3.3, 9.6)
4″		3.84 *bd* (2.8)	3.77 *bd* (3.3)
5″		3.48 *t* (6.1)	3.64 *t* (6.4)
6″a		3.58 *dd* (6.4, 11.3)	3.44 *dd* (6.8, 10.2)
6″b		3.65 *dd* (5.8, 11.2)	3.73 *dd* (5.6, 10.1)
1‴			4.51 *bs*
2‴			3.56 *bs*
3‴			3.48 *dd* (3.3, 9.5)
4‴			3.26 *t* (9.5)
5‴			3.51 *dd* (6.1, 9.3)
6‴			1.02 *d* (6.1)

Table 2. ^{13}C NMR spectral data for compounds **6**, **8** and **9** (DMSO-d_6, 125 MHz)

C	6	8	9
2	156.2	156.3	156.7
3	135.8	133.1	133.3
4	175.9	177.3	177.6
5	160.7	161.2	161.4
6	98.2	98.6	98.9
7	163.9	164.1	164.4
8	93.6	93.6	94.0
9	158.8	156.1	156.6
10	103.0	103.9	104.2
OCH_3	55.8	56.2	56.2
1′	122.0	121.0	121.3
2′	111.7	113.8	113.7
3′	146.6	146.9	147.2
4′	147.4	149.3	149.7
5′	115.6	115.3	115.4
6′	121.7	122.1	122.2
1″		101.6	102.0
2″		71.5	71.4
3″		73.0	73.2
4″		68.2	68.5
5″		76.1	73.8
6″		60.5	65.5
1‴			100.3
2‴			70.6
3‴			70.8
4‴			72.1
5‴			68.2
6‴			18.1

(1*R*,7*S*)-Germacra-4(15)-5,10(14)-trien-1β-ol (**3**). Oil, $[\alpha]_D^{25}$ −134.6° ($CHCl_3$; *c* 1.0). IR γ_{max}^{film} cm^{-1}: 3367, 3073, 2952, 2932, 2870, 1642, 1608, 1458, 1383, 1366, 1274, 1189, 1122, 1076, 1038, 1010, 996, 971, 929, 888, 848, 808; UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 237.8 (3.9); EIMS (probe) 70 eV, *m/z* (rel int.): 220 $[M]^+$ (2), 202 (14) 187 (6), 177 (21), 159 (47), 149 (15), 135 (29), 131 (29), 121 (29), 109 (100), 107 (48), 105 (39), 93 (49), 91 (84), 81 (53), 69 (33), 67 (41), 55 (48), 53 (26), 43 (54), 41 (73); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.81 (3H, *d*, J = 6.6 Hz, H-12), 0.88 (3H, *d*, J = 6.6 Hz, H-13), 1.48 (1H, *oct*, J = 6.6 Hz, H-11), 1.64 (2H, *m*, H-8a and 9a), 1.70 (1H, *ddd*, J_1 = 4.0 Hz, J_2 = 5.3 Hz, J_3 = 11.6 Hz, H-2a), 1.79 (1H, *m*, H-7), 2.03 (2H, *m*, H-2b and H-8b), 2.18 (1H, *ddd*, J_1 = 2.9 Hz, J_2 = 5.5 Hz, J_3 = 12.8 Hz, H-3a), 2.42 (1H, *dt*, J_1 = 4.8 Hz, J_2 = 12.8 Hz, H-3b), 2.62 (1H, *m*, H-9b), 3.76 (1H, *dd*, J_1 = 11.6 Hz, H-1), 4.83 (1H, *s*, H-15a), 4.91 (1H, *s*, H-15b), 4.99 (1H, *s*, H-14a), 5.26 (1H, *s*, H-14b), 5.42 (1H, *dd*, J_1 = 10.4 Hz, J_2 = 15.9 Hz, H-6), 5.99 (1H, *d*, J = 15.9 Hz, H-5); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.6 (C-12), 20.8 (C-13), 30.0 (C-3), 31.9 (C-11), 34.6 (C-9), 36.2 (C-2), 36.3 (C-8), 52.6 (C-7), 76.1 (C-1), 110.6 (C-14), 113.0 (C-15), 129.7 (C-5), 138.0 (C-6), 146.8 (C-4), 153.5 (C-10).

Alkaline hydrolysis of **2**

2 (20 mg) was saponified with KOH–MeOH for 2 h at room temp. The reaction mixture was processed in the usual way and **3** was obtained.

Acetylation of **3**

Compound **3** (20 mg) was treated overnight with Ac_2O and pyridine at room temp. The reaction mixt. was worked-up to give **2**.

Achillyl alcaneate (**4**). Oil IR γ_{max}^{film} cm^{-1}: 2985, 2854, 1734, 1645, 1450, 1377, 1243, 1164, 1112, 998, 893,

850, 721; UV λ_{max}^{MeOH} nm (log ε): 205.6 (3.6); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80 (3H, *s*, H-25), 0.87 (3H, *t*, J = 7.1 Hz, Me′), 0.94 (3H, *s*, H-26), 1.30 (*bs*, $_2$), 1.60 (12H, *bs*, H-24, H-28, H-29, H-30), 1.67 (3H, *bs*, H-23), 2.03 (19H, *m*), 2.29 (2H, *t*, J = 7.4 Hz, H-2′), 4.62 (1H, *bs*, H-27a), 4.67 (1H, *dd*, J_1 = 8.3 Hz, J_2 = 4.1 Hz, H-3), 4.87 (1H, *bs*, H-27b), 5.12 (4H, *m*, H-10, H-13, H-17, H-21); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH_3'), 16.1 (C-30), 16.1 (C-29), 16.1 (C-24), 17.7 (C-28), 18.3 (C-25), 22.7 (CH_2'), 24.2 (C-7), 25.2 (C-3′), 25.7 (C-23), 26.3 (C-26), 26.8 (C-11), 26.9 (C-12), 28.3 (C-20), 28.4 (C-16), 28.8 (C-2), 29.3 (CH_2'), 29.4 (CH_2'), 29.6 (CH_2'), 29.7 (CH_2'), 29.7 (CH_2'), 29.8 (CH_2'), 31.3 (CH_2'), 32.0 (C-1) 34.9 (C-2′), 38.6 (C-8), 39.2 (C-4), 39.8 (C-19), 39.8 (C-15), 51.6 (C-5), 78.3 (C-3), 109.3 (C-27), 124.4 (C-10, C-13), 124.5 (C-17, C-21), 131.2 (C-22), 134.9* (C-9) 135.2* (C-14), 135.3* (C-18), 147.0 (C-6, 173.4 (C-1′). *Interchangeable values.

Saponification of **4** (KOH–MeOH) yielded an alcohol whose spectral data where identical to those of an authentic sample of achilleol A. The acid fraction esterified with CH_2N_2 was analyzed by GC and dodecanoic, tetradecanoic and hexadecanoic acids were identified.

Z-8-Decene-4,6-diyn-1-ol (**5**). Oil IR γ_{max}^{film} cm^{-1}: 3463, 3010, 2925, 2854, 2331, 2299, 1660, 1458, 1435, 1363, 1248, 1197, 1171, 1116, 1016, 721, 665; UV λ_{max}^{MeOH} nm (log ε): 205.2 (4.5), 247.8 (3.7), 250.8 (4.0), 258.8 (3.9), 265.8 (4.1), 275.8 (4.2), 281.2 (4.1); EIMS (probe) 70 eV, *m/z* (rel. int.): 148 $[M]^+$ (71), 147 (21), 133 (43), 131 (6), 130 (21), 128 (66), 127 (27), 119 (11), 115 (99), 103 (66), 91 (100), 77 (97), 63 (45); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.77 (2H, *tt*, J = 6.6 Hz, H-2), 1.87 (3H, *dd*, J_1 = 1.7 Hz, J_2 = 6.9 Hz, H-10), 2.44 (2H, *t*, J = 7.0 Hz, H-3), 3.72 (2H, *t*, J = 6.1 Hz, H-1), 5.46 (1H, *dd*, J_1 = 1.7 Hz, J_2 = 10.8 Hz, H-8), 6.08 (1H, *dq*, J_1 = 7.0 Hz, J_2 = 10.8 Hz, H-9); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.2 (C-3), 16.4 (C-10), 31.0 (C-2), 61.4 (C-1), 65.7 (C-5), 72.2 (C-7), 78.4 (C-6), 83.9 (C-4), 109.1 (C-8), 142.5 (C-9). From the EtOAc extract (14.97 g), tamarixetin (**6**) precipitated and was recrystallized in hexane (400 mg). The mother liquors were chromatographed over silica gel with hexane to afford 98 frs. Frs 68–74 were recrystallized in hexane to yield **7** (939 mg).

(*E,E*)-Pentadeca-5,7-diene-9,11,13-triyn-2-one (**7**). Yellow solid, mp 65–67° (hexane). IR γ_{max}^{KBr}: 3020, 2925, 2854, 2234, 2205, 2177, 1708, 1628, 1582, 1431, 1405, 1357, 1288, 1159, 1021, 984, 933, 785, 731, 609; UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 204.4 (3.6), 225.0 (2.7), 258.8 (3.8), 263.8 (3.6), 268.8 (4.1), 279.6 (3.1), 289.0 (3.2), 293.8 (3.1), 305.6 (3.5), 312.6 (3.2), 325.4 (3.7), 334.4 (3.1), 348.0 (3.6); EIMS (probe) 70 eV, *m/z* (rel. int.): 210 $[M]^+$ (7), 195 (9), 182 (11), 167 (51), 165 (60), 152 (100), 139 (14), 126 (11), 115 (9), 98 (6), 87 (7), 74 (9), 63 (8), 51 (7), 43 (63); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (3H, *s*, H-15), 2.12 (3H, *s*, H-1), 2.36 (2H, *q*, J = 7.1 Hz, H-4), 2.53 (2H, *t*, J = 7.2 Hz, H-3), 5.48 (1H, *d*, J = 15.5 Hz, H-8), 5.83 (1H, *dt*, J_1 = 7.2 Hz, J_2 = 15.2 Hz, H-5), 6.10 (1H, *dd*, J_1 = 10.8 Hz, J_2 = 15.2 Hz, H-6), 6.68 (1H, *dd*, J_1 = 10.8 Hz, J_2 = 15.5 Hz, H-7); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.7 (C-15), 26.8 (C-4), 30.0 (C-1), 42.5 (C-3), 59.3* (C-10), 65.0* (C-11), 68.2* (C-12), 75.3 (C-9), 76.7* (C-13), 78.7 (C-14), 107.7 (C-8), 130.3 (C-6), 138.2 (C-5), 146.3 (C-7), 207.4 (C-2). *Interchangeable values.

The EtOH extract (12.25 g) was partitioned between BuOH and H_2O. The BuOH extract (8.9 g) was subjected to silica gel CC (EtOAc–EtOH–H_2O, 20:4:1) to give 17 frs. After precipitation of fr. 1 and fr. 3 with hexane, compounds **8** (270 mg) and **9** (400 mg) were isolated. Fr. 7 afforded 1.35 g of ribitol.

Tamarixetin 3-robinobioside (**9**). Yellow solid, mp 186–188° (hexane), $[\alpha]_D^{25}$ −17.5° (MeOH; *c* 0.1). IR γ_{max}^{KBr} cm^{-1}: 3404, 1653, 1600, 1562, 1507, 1291, 1206, 1169, 1130, 1056, 1032, 983; UV λ_{max}^{MeOH} nm (log ε): 204.6 (3.6), 237.2 (3.0), 254.2 (3.3), 286.6 (1.0), 371.4 (3.3); EIMS (probe) 70 eV, *m/z* (rel. int.): 345 [M–Fuc–Gal]$^+$ (13), 318 (17), 317 [M–Fuc–Gal–CO] (100), 316 (28), 138 (12), 137 (7), 129 (19), 85 (11).

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