Phytochemistry, Vol 28, No 10, pp. 2773–2776, 1989.
Printed in Great Britain

0031–9422/89 $3.00+0.00

TRITERPENE GLYCOSIDES FROM *MUSSATIA* SPECIES

CARLOS JIMÉNEZ, MARY CARMEN VILLAVERDE, RICARDO RIGUERA, LUIS CASTEDO* and FRANK STERMITZ†

Departamento de Química Orgánica del la Facultad de Química y Sección de Alcaloides del CSIC, Santiago de Compostela, Spain, †Department of Chemistry, Colorado State University, Fort Collins, CO 80523, U S A

(*Received* 6 *February* 1989)

Key Word Index—*Mussatia* sp nov, *M hyacinthina*, Bignoniaceae, bark, triterpenes; saponins

Abstract—The *E*-dimethylcaffeic and *E*-*p*-methylcoumaric esters of 3β-*O*-[*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl]-21β-hydroxyolean-12-en-28-oic acid, and 3β-*O*-[O-β-D-xylopyranoxyl-(1→3)-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl]-21β-hydroxyolean-12-en-28-oic acid were isolated from the methanolic extracts of *Mussatia* sp. nov and *M. hyacinthina* and their structures determined on the basis of chemical and spectral evidence.

INTRODUCTION

In previous papers [1–3], we have reported the isolation of a series of new phenylpropanoid glycosides from two *Mussatia* species used in Central and South American folk medicine (preliminary pharmacological studies of these compounds suggest that they inhibit LTB_4 formation). In continuance of our research on the members of this genus, we now wish to report our results concerning a triterpene-glycoside-containing fraction isolated from the bark of *Mussatia* sp. nov and *M hyacinthina*.

RESULTS AND DISCUSSION

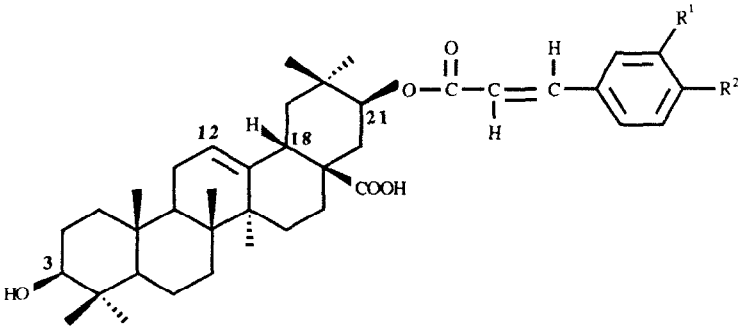
From the methanolic extracts of the bark of *Mussatia* sp. nov and *M hyacinthina* we isolated a complex mixture of triterpene glycosides which was subjected to several seperation techniques (DCCC, RLCC, HPLC, Sephadex, etc) without completely satisfactory results. The ^1H and ^{13}C NMR spectra of a fraction, shown by HPLC to consist of a poorly resolved mixture of four major components, presented signals due to three sugars, one *N*-acetyl group, seven methyl groups indicative of an oleanane type triterpene skeleton, and dimethylcaffeic and *p*-methylcoumaric ester functions In an effort to identify the components and elucidate their structures we resorted to analysis of the products resulting from selective acid and basic hydrolyses Treatment of the mixture of glycosides with 2 M hydrochloric acid gave glucose, xylose and glucosamine From the organic phase we obtained, after HPLC separation, the triterpene esters **1** and **2**

The molecular formula of **1** was determined as $C_{41}H_{58}O_7$ by HR-FAB-mass spectrometry. Its IR spectrum exhibited absorption bands at 3400 (OH), 1699 (CO), 1633 (CH=CH) and 1600 and 1513 cm^{-1} (arom.). The ^1H NMR spectrum showed the presence of two aromatic methoxy groups at δ3.92 and 3.91, an ABX system at δ6.86 (1H, *d*, J_o=8.4 Hz), 7.05 (1H, *d*, J_m=1.7 Hz) and 7.10 (1H, *dd*, J_m=1.7 Hz and J_o=8.4 Hz) and an AB system at 6.27 and 7.59 (J=15.9 Hz), which revealed the existence of an *E*-dimethyl caffeoyl group in **1**. The LREI mass spectrum of **1** showed a fragment at *m/z* 454 ($C_{30}H_{46}O_3$) generated from the $[M]^+$ (absent in this spectrum) through a McLafferty rearrangement with loss of a dimethyl caffeoyl group. The presence of significant fragments at *m/z* 208 and 246, resulting from the retro-Diels–Alder cleavage of the radical ion at *m/z* 454, suggested that **1** was a Δ^{12}-unsaturated triterpene [4]. This was confirmed by both the ^{13}CNMR and the ^1H NMR spectra showing signals for C-12 (δ122.63), C-13 (δ142.29) and H-12 (δ5.34) [5]. The existence of an equatorial free secondary hydroxy group at C-3 was supported by ^1H NMR [δ3.22 (1H, *dd*, J=3.5 and 11.1 Hz)] and by ^{13}C NMR [78.99 (C-3), 27.59 (C-2), 38.71 (C-4), 28.67 (C-23) and 15.44 (C-24)], while the equatorial orientation of the *E*-dimethylcaffeoyl group at C-21 was deduced by comparison with published data for **3** [6]. Finally, H-18 was shown to be equatorial by its chemical shift (δ2.93) and double doublet coupling (J_{aa} = 14.0 Hz and J_{ae} = 3.8 Hz). Thus, the structure of **1** was established as 3β-hydroxy-21β-*E*-dimethylcaffeoyloxy-olean-12-en-28-oic acid

The ^1H NMR, mass and IR spectral data of **2** were very similar to those of **1**. Compound **2** showed two AB systems, one belonging to a *trans* double bond at δ6.27 and 7.60 (J=15.9 Hz) and the other to four aromatic protons at δ7.47 and 6.89 (J=8.8 Hz). Together with the singlet at δ3.83 due to the methoxy group, this supported the presence of an *E*-*p*-methoxycinnamoyl unit in compound **2** instead of the *E*-dimethylcaffeoyl present in **1**. The remaining signals in the ^1H NMR of compound **2** were essentially the same as those of **1**. Thus, the structure of **2** was established as 3β-hydroxy-21β-*E*-*p*-methoxycinnamoyloxyolean-12-en-28-oic acid.

Basic hydrolysis of the mixture of triterpene glycosides with 2 M NaOH brought about the cleavage of the ester and acetamide groups, after which HPLC separation afforded compounds **4a** and **5** along with a very small quantity of **4b**.

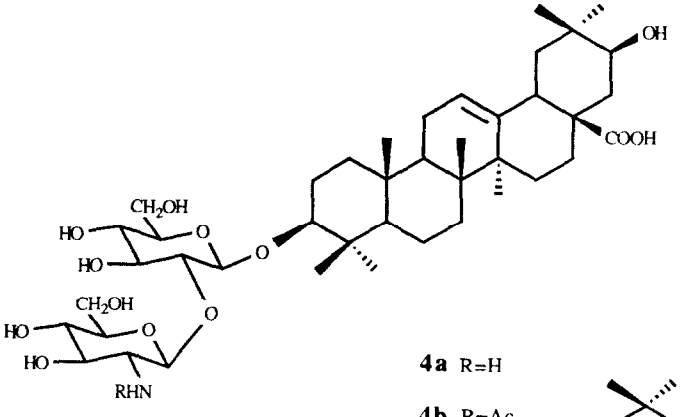
The molecular weight and the sequence of sugars in **4a** were deduced from its negative-ion FAB-mass spectrum, which showed signals at *m/z* 794 $[M-H]^-$, 633 $[M-H-161]^-$ (corresponding to the loss of a terminal glucosamine) and 471 $(M-H-161-162]^-$ (due to the loss of one glucosamine and one glucose). The presence of these



1 $R^1 = R^2 = OMe$

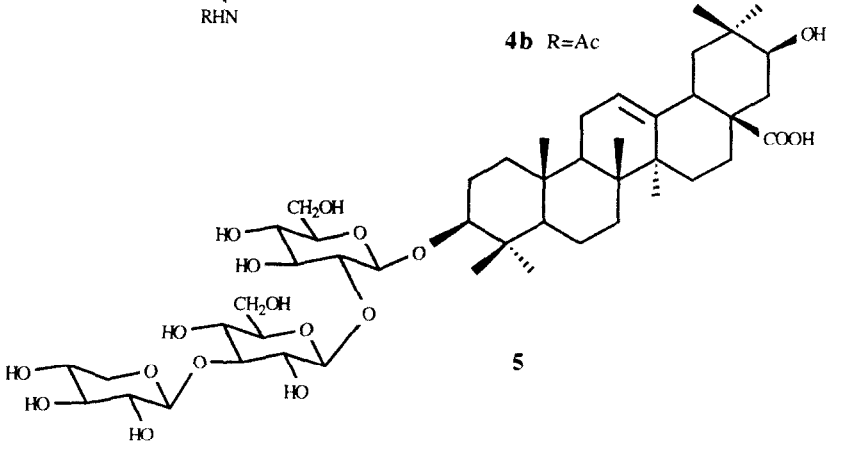
2 $R^1 = H$ $R^2 = OMe$

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



4a R=H

4b R=Ac



5

two sugars in **4a** was confirmed by ^1H and ^{13}C NMR, since the anomeric proton of glucosamine resonated at δ4 70 and exhibited the expected coupling to its vicinal proton (geminal to the nitrogen) at δ2.55, as was observed by COSY-45 and decoupling resonance. Furthermore, C-2 of glucosamine resonates under ^{13}C NMR at δ59 15. The remaining signals were in good agreement with the data reported in the literature [7, 8] for other amino sugar-containing triterpene glycosides. The interglycosidic linkages and the point of attachment of the sugar chain to the aglycone were established by ^{13}C and ^1H NMR spectroscopy Comparison of the downfield shifts of the glucose moiety, C-2 (δ80.15) and H-2 (δ3 60) signals with those of methyl glucopyranoside [9] indicated that the glucosamine is linked to C-2 of glucose That the sugar chain is linked to the aglycone at C-3 is deduced from C-3 signal at δ91 89 in the ^{13}C NMR spectrum [10]. Finally, comparison of the NMR data of the aglycone moiety of **4a** with those of **1** and **2** clearly indicates that the oleanane skeleton in **4a** has a free

hydroxyl group at C-21, and this was confirmed by HREI mass spectrometry. Thus, **4a** is 3β-*O*-[*O*-2-amino-2-deoxy-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl]-21β-hydroxyolean-12-en-28-oic acid.

The negative ion FAB mass spectrum of **4b** shows a $[M]^+$ at *m/z* 836 $[M-H]^-$ and other significant fragments at *m/z* 633 $[M-H-203]^-$ (corresponding to the loss of *N*-acetylglucosamine) and 471 $[M-H-203-162]^-$ (corresponding to the loss of *N*-acetylglucosamine and one glucose unit). The remaining fragments are coincident with those of compound **4a**, and so compound **4b** is 3β-*O*-[*O*-2-acetamido-2-deoxy-β-D-glycopyranosyl-(1→2)-β-D-glucopyranosyl]-21β-hydroxyolean-12-en-28-oic acid

The negative ion FAB mass spectrum of **5** showed a $[M]^+$ at *m/z* 927 $[M-H]^-$ together with signals at *m/z* 795 $[M-H-132]^-$ (due to the loss of a terminal xylose unit) and 633 $[M-H-132-162]^-$ and $[M-H-132-162-162]^-$ (corresponding to the sequential loss of xylose and one glucose unit and xylose and two glucose units respectively) The FAB mass spectrum (positive ion spectrum) showed a $[M]^+$ at *m/z* 951 $[M+Na]^+$ and a fragment at *m/z* 882 due to the loss of COOH. The ^1H and ^{13}C NMR data of **5** were almost identical to those of **4a** except for the signals belonging to the sugars. The aglycone is the same as in **4** (as was confirmed by HREI mass spectrometry), with the sugar chain likewise linked to C-3 of the triterpene The interglycosidic linkages between the sugar units were established by comparison of the NMR data with those reported in the literature [9]. In the ^{13}C NMR spectrum, the signals at δ62.44 and 62.79 correspond to C-6 of the two glucose units and show that these hydroxyl groups are free, while the signals at δ80.86 and 87.83 indicate that the two glucose units are bound via C-2 and C-3 The downfield shift of H-2 in both glucoses as observed by COSY-45 served to confirm this. Thus the structure of **5** is 3β-*O*-[*O*-β-D-xylopyranoxyl-(1→3)-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl]-21β-hydroxyolean-12-en-28-oic acid. In accordance with these results we concluded that the triterpene glycosides isolated from *Mussatia* sp nov. and *M. hyacinthina* species are the *E*-dimethylcaffeic and *E*-*p*-methylcoumaric esters of **4b** and **5.**

EXPERIMENTAL

^1H and ^{13}C NMR were recorded at 250 and 62 8 MHz, respectively HRMS (FAB) was performed by the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, U S A The negative ion FABMS spectra were performed by the Dipartamento di Chimica delle Sostanze Naturali, Napoli, Italy LREIMS, LRCIMS and HREIMS were recorded on a magnetic sector apparatus HPLC sepns were performed on a Whatman Partisil ODS column using an instrument equipped with an UV detector operating at 254 nm and a R401 differential refractometer

Plant materials. Extn and isolation was carried out on bark of *Mussatia* sp nov [1] and *M hyacinthina* [3] from Peru

Extraction and isolation The procedure previously reported [1–3] for the isolation of phenylpropanoid glycosides was followed Bark of *Mussatia* sp nov (290 g) was defatted with hexane and the residue extracted with MeOH and then lyophilized to give 72 g of powder This extract (45 g) was worked-up as before [1, 2], partitioning between H_2O and H_2O–satd *n*-BuOH affording, after concn under red pres., 5 3 and 24.8 g, respectively Passing the *n*-BuOH extract through a column of neutral Al_2O_3 [1] gave 17.05 g An 8 g sample was fractionated by RLCC [1, 2] and the stationary phase gave 800 mg of a mixt of triterpene glycosides. Similar processing of the bark of *M. hyacinthina* (45 g) produced 120 mg of a mixt of triterpene glycosides

Acid hydrolysis, isolation of **1** and **2.** The mixt of triterpene glycosides (124 mg) was refluxed in aq 2 M HCl for 3 hr This soln was dild with H_2O, extracted with $CHCl_3$ and the $CHCl_3$ evapd off The residue (62 mg) was first purified by prep TLC (silica gel, $CHCl_3$–MeOH–H_2O, 13 7:2) and then sepd by HPLC (reverse phase, MeOH–H_2O, 2 23) to give pure compounds **1** (15 mg) and **2** (6 mg). In the aq layer were identified glucose, xylose and glucosamine.

3β-Hydroxy-21β-E-dimethylcaffeoyloxyolean-12-en-28-oic acid **(1).** $[\alpha]_D$ −21° ($CHCl_3$, *c* 0 10); IR (neat) ν_{max} cm^{-1} 3400, 2942, 1699, 1633, 1600, 1513, 1258; ^1H NMR ($CDCl_3$) *E*-dimethylcaffeoyl group δ3 91 (3H, *s*, OMe-4'), 3 92 (3H, *s*, OMe-3'), 6.27 (1H, *d*, *J* = 15.9 Hz, H-8'), 6.86 (1H, *d*, J_o = 8 4 Hz, H-5'), 7.05 (1H, *d*, J_m = 1 7 Hz, H-2'), 7.10 (1H, *dd*, J_o = 8 4 Hz and J_m = 1 7 Hz, H-6'), 7 59 (1H, *d*, *J* = 15.9 Hz, H-7'); triterpene δ0 74, 0 77, 0 91, 0.93, 0 98, 1 07, 1.14 (3H each, *s*, Me), 1 35 and 1 90 (1H each, *m*, H-19), 1 70 and 1 80 (1H each, *m*, H-22), 1 60 (2H, *m*, H-2), 1.85 (2H, *m*, H-11), 2 93 (1H, *dd*, *J* = 3.8 and 14 0 Hz, H-18), 3 22 (1H, *dd*, *J* = 3 5 and 11 1 Hz, H-3), 4.94 (1H, *dd*, *J* = 4.7 and 11 9 Hz, H-21), 5 34 (1H, *m*, H-12) ^{13}C NMR ($CDCl_3$) *E*-dimethylcaffeoyl group δ55.21 (OMe), 55 92 (OMe) 109 84 (C-5'), 111.16 (C-2'), 116 10 (C-8'), 123.50 (C-6'), 127 50 (C-1'), 144 65 (C-7'), 149.36 (C-3'), 151 26 (C-4'), 166.83 (C-9'). triterpene see Table 1. LREIMS *m/z* (rel. int.) 454 $[M-C_{11}H_{12}O_4, 7\,4]^+$, 436 $[454-H_2O, 3\,7]$, 408 [454 − HCOOH, 5.9], 246 (100) 208 (85 2), 201 [246 − COOH, 77 0], 190 (50 4), 191 (13.8) LRCIMS *m/z* (rel int) 662 (M^+, 8), 645 (48), 455 (9), 437 (50), 409 (9), 247 (18), 209 (98), 191 (100) HRFABMS *m/z* (rel. int): 662.4186 (Calc 662 4182) (M^+, 3 7), 454 $[M-C_{11}H_{12}O_4, 0.3]^+$, 409 [454 − COOH, 0 9], 246 (0.7), 208 (2), 201 [246 − COOH, 1.1], 191 (13 8).

3β-Hydroxy-21β-E-p-methoxycinnamoyloxyolean-12-en-28-oic acid **(2).** $[\alpha]_D$ −23° ($CHCl_3$; *c* 0.10); IR ν_{max}^{neat} cm^{-1}: 3400, 2946, 1700, 1634, 1604, 1512, 1171; ^1H NMR ($CDCl_3$) *E*-*p*-methoxycinnamoyl group. δ3 83 (3H, *s*, OMe-4'), 6.27 (1H, *d*, *J* = 15.9 Hz, H-8'), 6.89 (2H, *d*, *J* = 8 8 Hz, H-3' and H-5'), 7.47 (2H, *d*, *J* = 8 8 Hz, H-2' and H-6'), 7.60 (1H, *d*, *J* = 15 9 Hz, H-7'); triterpene. δ0.74, 0 76, 0.91, 0.92, 0.98, 1 05, 1.14 (3H each, *s*, Me), 2 93 (1H, *dd*, H-18), 3.22 (1H, *dd*, H-3), 4.92 (1H, *dd*, *J* = 4.7 and 11.4 Hz, H-21), 5.33 (1H, *m*, H-12) LRCIMS *m/z* (rel int): 631 $[M-H, 10]^+$, 455 $[M-C_{11}H_{12}O_4, 12]^+$, 437 (50), 409 [454 − COOH, 6], 247 (12), 209 (11), 201 [246 − COOH, 6], 191 (60), 179 (98), 161 (100)

Basic hydrolysis, isolation of **4a**, **4b** *and* **5.** The original of triterpene glycosides (200 mg) was refluxed in a 10% soln of KOH in MeOH for 6 hr, then H_2O was added and the mixt. extd with Et_2O *E*-Dimethylcaffeoyl and *E*-*p*-methoxycinnamoyl acids were isolated from the organic layer The aq. layer was neutralized with HCl and concd under red pres. and the residue (51 mg) subjected to HPLC (reverse phase, MeOH–H_2O, 3 2) to give the saponins **4a** (15 mg), **4b** (2 mg) and **5** (10 mg)

3β-O-[O-2-amino-2-deoxy-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl]-21β-Hydroxyolean-12-en-28-oic acid **(4a)** $[\alpha]_D$ +12° (MeOH, *c*, 0 28). ^1H NMR (CD_3OD) aglycone moiety δ0 74, 0 77, 0 91, 0 93, 0 98, 1 07, 1.14 (3H each, *s*, Me), 1.20, 1 70 (2H, *m*, H-19), 1 6 (2H, *m*, H-2), 1 80 (2H, *m*, H-11), 2 93 (1H, *dd*, *J* = 3 8 and 14 0 Hz, H-18), 3 44 (1H, *m*, H-3), 5.22 (1H, *m*, H-12); glucose moiety δ4 41 (1H, *d*, *J* = 7 1 Hz, H-1), 3 60 (1H, *m*, H-2), 3 43 (1H, *m*, H-3), 3 25 (1H, *m*, H-5), 3 84 (1H, *dd*, *J* = 5 0 and 10 0 Hz, H-6a), 3.60 (1H, *m*, H-6b); glucosamine moiety. δ4.67 (1H, *d*, *J* = 7 8 Hz, H-1), 2 55 (1H, *dd*, *J* = 7 8 and 8 6 Hz, H-2), 3.18 (1H,

Table 1 ^{13}C NMR chemical shift data of the triterpene skeleton of compounds **1**, **4a** and **5**

	1[a]	4a[b]	5[b]
C-1	38 41	39 87	39 91
C-2	27 59	27 09	27 17
C-3	78 99	91 89	91 78
C-4	38.71	40.45	40 42
C-5	55 21	57 16	57 29
C-6	18 22	19 40	19 40
C-7	32 64	34 21	34 24
C-8	39 25	40 56	40.57
C-9	47.58	47.98	47 98
C-10	37 04	37 94	37 94
C-11	23 38	24 57	24 58
C-12	122 63	122 98	123.07
C-13	142 29	145.75	145 70
C-14	41 60	40 56	40 57
C-15	27 13	29 34	29 34
C-16	24 11	25 87	25 86
C-17	48 04	c	c
C-18	40.48	43.05	43 05
C-19	46 41	46 22	46 24
C-20	35 26	37 27	37.26
C-21	75.01	72 47	73.06
C-22	36 40	42 17	42 15
C-23	28 67	28 44	28 24
C-24	15 45	16 89	16 61
C-25	15 26	15 92	15 95
C-26	17 05	17 78	17.77
C-27	25.71	26.30	26 30
C-28	181 00	179 50	180 10
C-29	28 04	29 90	29 88
C-30	18 34	18 22	18 18

a In $CDCl_3$
b In CD_3OD
c Obscured by the solvent

m, H-3), 3 25 (1H, *m*, H-5), 3 84 (1H, *dd*, $J = 5$ 0 and 10.0 Hz, H-6a), 3 60 (1H, *m*, H-6b) ^{13}C NMR (CD_3OD): δaglycone moiety. see Table 1, glucose moiety: δ62 95 (C-6), 71.69 (C-4), 77 74 (C-5), 78 83 (C-3), 80 15 (C-2), 105 49 (C-1); glucosamine moiety· δ59 15 (C-2), 63 54 (C-6), 74 78 (C-4), 77 75 (C-3), 78 57 (C-5), 104 35 (C-1). HREIMS *m/z* Found (Calc., rel int.) *m/z* 400–500 454 3446 (454 3447, $C_{30}H_{46}O_3$, 11 9), 437.3331 (437 3419, $C_{30}H_{45}O_2$, 100), 436.33411 (436.33411, $C_{30}H_{44}O_2$, 71 6), 421 30190 (421 31064, $C_{29}H_{41}O_2$, 43 2), *m/z* 150–400· 246.16650 (246 16197, $C_{16}H_{22}O_2$, 25 6), 201 16640 (201.16432, $C_{15}H_{21}$, 100), 190 17250 (190 17214, $C_{14}H_{22}$, 31 3), 175 14900 (175 14867, $C_{13}H_{19}$, 22.6) FABMS (negative ion) *m/z* (rel int.). 794 ($[M-H]^-$, 100), 633 ($[M-H-161]^-$, 75), 471 ($[M-H-161-162]^-$, 60)

3β-O-[O-2-*amino*-2-*deoxy*-β-D-*glucopyranosyl*-(1→2)-β-D-*glucopyranosyl*]-21β-*Hydroxyolean*-12-*en*-28-*oic acid* (**4b**) FABMS (negative ion) *m/z* (rel. int) 836 $[M-H]^-$, 100), 633 ($[M-H-203]^-$, 35), 471 ($[M-H-203-162]^-$, 35)

3β-O-[O-β-D-*xylopyranoxyl*-(1→3)-O-β-D-*glucopyranosyl*]-21β-*Hydroxyolean*-12-*en*-28-*oic acid* (**5**) $[\alpha]_D$ +8° (MeOH, *c* 0 20) ^1H NMR (CD_3OD). aglycone moiety· δ0.82, 0 83, 0 89, 0 91, 0 92, 1.03. 1 11, (3H each, *s*, aliphatics Me), 1 20, 1 70 (2H, *m*, H-19), 1.60 (2H, *m*, H-2), 1 80 (2H, *m*, H-11), 2.92 (1H, *dd*, H-18), 3 35 (1H, *m*, H-3), 5 21 (1H, *m*, H-12), glucose moiety I δ4 41 (1H, *d*, $J = 7$ 4 Hz, H-1), 3 58 (1H, *m*, H-2), glucose moiety II δ4 61 (1H, *d*, $J = 7$ 6 Hz, H-1), 3.35 (1H, *m*, H-2), xylose moiety; δ4 78 (1H, *d*, $J = 7$ 7 Hz), 3 20 (1H, *m*, H-2) ^{13}C NMR (CD_3OD) δaglycone moiety see Table 1, glucose units δ62 44 (C-6), 62 79 (C-6), 70.23 (C-4) 71 51 (C-4), 75 26 (C-2 and C-3), 77 18 (C-5), 78 36 (C-5), 80.86 (C-2), 87 82 (C-3), 104 56 (C-1), 104 02, (C-1); xylose moiety· δ66 95 (C-5), 70 41 (C-4), 74 76 (C-2), 76 18 (C-3), 105 69 (C-1) HREIMS *m/z* (rel int). 454 34467 ($C_{30}H_{46}O_3$, 1 1), 437 33194 ($C_{30}H_{45}O_2$, 3 7), 436.33220 ($C_{30}H_{44}O_2$, 3 6), 421 31064 ($C_{29}H_{41}O_2$, 2 2), 408 33920 ($C_{29}H_{44}O$, 0 8), 393 31572 ($C_{28}H_{41}O$, 2 5), 246 16197 ($C_{16}H_{22}O_2$, 43 6), 201 16432 ($C_{15}H_{21}$, 100), 190 17214 ($C_{14}H_{22}$, 65 2), 175 14867 ($C_{13}H_{19}$, 32 0) FABMS (negative ion) *m/z* (rel int.) 927 ($[M-H]^-$, 100), 795 ($[M-H-132]^-$, 50), 633 ($[M-H-132-162]^-$, 45), 471 ($[M-H-132-162-162]^-$, 45) FABMS (positive ion) *m/z* (rel int) 973 ($[M-H+2Na]^+$, 68), 951 ($[M+Na]^+$, 98), 905 ($[M-HCOOH+Na]^+$, 100), 882 ($[M-COOH]^+$, 60)

Acknowledgements—This work was supported by the U S -Spain Joint Committee for Scientific and Technological Cooperation (Grant CCB-8402/006) and by an F P I grant awarded by the Spanish Ministry of Education and Science to C J G We thank the Midwest Center for Mass Spectroscopy for HRFAB and FAB mass spectra We are also grateful to Prof Minale for helpful discussions

REFERENCES

1 Jiménez, C, Villaverde, M C, Riguera, R, Castedo, L and Stermitz, F R (1987) *Phytochemistry* **26**, 1805
2 Jiménez, C, Villaverde, M C, Riguera, R., Castedo, L and Stermitz, F R (1988) *Phytochemistry* **27**, 2947
3 Jiménez, C, Villaverde, M C, Riguera, R, Castedo, L and Stermitz, F R (1989) *J Nat Prod* **52**, 408
4. Ogunkoya, L (1981) *Phytochemistry* **20**, 121.
5 Tori, K., Seo, S, Yoshimura, Y, Nakamura, M, Tomita, Y and Ishii, H (1976) *Tetrahedron Letters* 4167
6 Delgado, M C C, Da Silva, M S and Braz Fo, R (1984) *Phytochemistry* **23**, 2289
7 Ripperger, H, Preiss, A and Schmidt, J (1981) *Phytochemistry* **20**, 2434
8. Okada, Y, Shibata, S, Ikekawa, T, Javaellana, A M. J and Kamo, O (1987) *Phytochemistry* **26**, 2789
9 Bock, K and Pedersen, C (1983) *Adv Carbohydr Chem Biochem* **41**, 27
10 Tori, K, Seo, S, Shimaoka, A and Tomita, Y (1974) *Tetrahedron Letters* 4227