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LIMONOID EXTRACTIVES FROM *TURRAEA FLORIBUNDA* AND *T. OBTUSIFOLIA*

JOHN A. AKINNIYI, JOSEPH D. CONNOLLY, DULCIE A. MULHOLLAND*, DAVID S. RYCROFT and DAVID A. H. TAYLOR*

Department of Chemistry, University of Glasgow, G128QQ, Scotland, U.K.; *Department of Chemistry, University of Natal, Durban, 4001, South Africa

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Key Word Index—*Turraea floribunda*; *T. obtusifolia* Meliaceae; limonoid; prieurianin.

Abstract—Extraction of the whole plant of *Turraea obtusifolia* has given prieurianin, a complex limonoid of known structure which is a useful taxonomic marker. Extraction of *Turraea floribunda* gave a mixutre of limonoids, apparently of the same group as prieurianin but of a lower oxidation state. Three of these have been isolated and the structure determined, mainly by spectroscopic methods.

INTRODUCTION

Turraea (Meliaceae) is a genus mostly of shrubs, widespread in Africa and the Indian Ocean islands. It is placed in the tribe Turraeeae, subfamily Meliodeae [1], where it is accompanied by a number of smaller related genera, and by the monotypic genus *Nymania*, which we have recently studied [2]. *Nymania* has been the cause of much botanical dispute, as it is superficially unlike other Meliaceae, but was found to contain prieurianin, a characteristic complex limonoid [3] of the genera *Trichilia* and *Guarea*.

Turraea obtusifolia (Hochstetter) is widely distributed in Southern Africa, although nowhere very common. We have extracted a plant provided by the Natal Forestry Department, and have isolated prieurianin, identified by comparison of the ^{1}H NMR spectra (at 60°) of the free compound and its acetate, as the only limonoid. This supports the taxonomic relationship with *Trichilia*, *Guarea* and *Nymania*, and the inclusion of all these species in the same sub-family. It does however appear that the two closely related genera *Melia* and *Azadirachta* which are placed in the same sub-family, assort badly with the other members.

Turraea floribunda (Hochstetter) is distributed throughout East Africa, being locally rather common. It has a white flower with a powerful scent at night, and is commonly known as a 'honeysuckle'. We have extracted a plant from the garden of Professor K. H. Pegel, and found it to contain a mixture of limonoids, on which we now report.

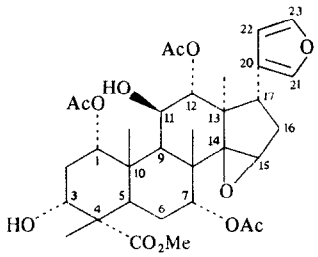
RESULTS AND DISCUSSION

Extraction of the ground bark of *T. floribunda* gave a gum which by column chromatography and preparative TLC gave two crystalline compounds **A** and **B**, and a third, **C**, which was amorphous. All were limonoids.

Compound **A**, $C_{33}H_{44}O_{12}$, contains a β-substituted furan, two hydroxyl groups, a methoxycarbonyl group, a trisubstituted epoxide, three acetate esters, (methyl resonance δ2.13, 2.12, 2.05), and four tertiary methyl groups. These account for all the oxygen atoms, and suggest a structure similar to that of the heudelottins [4] or hirtin [5], in which a methoxycarbonyl has replaced one of the angular methyl groups. In the normal limonoid skeleton, the 4α-methyl group is the only equatorial one, and as a result gives a characteristically wide ^{1}H NMR signal, and a characteristically downfield ^{13}C NMR signal. Since these are absent, we deduce that the methoxycarbonyl occupies the 4α-position. Double resonance experiments show that the vicinal proton (δ3.75) to one of the hydroxyl groups is coupled to two doublets at δ4.36 (J = 3 Hz) and 3.00 (J = 3 Hz). This is consistent with the 11β-hydroxyl, 12α-acetoxy arrangement which is common in limonoids. In limonoids containing cleaved B rings, a 12α-acetate group is so disposed that the acetate methyl is heavily shielded by the furan ring, and resonates at about δ1.5. However this is not so in compounds with the intact tetracyclic nucleus [4].

Oxidation of compound **A** with Collins' reagent gave a diketone which lost acetic acid to form a conjugated unsaturated ketone in which the vinyl proton resonances were at δ7.82 and 5.92 (J = 10 Hz). This corresponds to the values expected from an original 3-hydroxy-1-acetate, and not the isomeric 1-hydroxy structure. The unusually low field shift of H-1 is due to the deshielding effect of the 11-ketone, and also occurs in 11-ketocedrelone [D. A. H. Taylor, unpublished observation]. We therefore propose the structure **1** for compound **A**. Attempts at decarboxylation were unsuccessful, treatment with mineral acid caused an oxide rearrangement to **2**, similar to that observed in havanensin [6].

Compound **B**, $C_{37}H_{50}O_{13}$, was clearly closely related, the formula corresponding to that expected for an isobutyrate of compound **A**. Oxidation showed that the 3-hydroxyl was still present, and that an acetate was present at C-1. The normal shift (δ7.30) observed for H-1 in the unsaturated oxidation product confirmed the absence of the 11-ketone, and hence that hydroxyl-11 was acylated in compound **B**. Although it is not certain that the isobutyrate is at C-11, since the acetates may have rearranged, the consistency of the acetate methyl shifts in compounds **A** and **B** make it seem probable that this is so.



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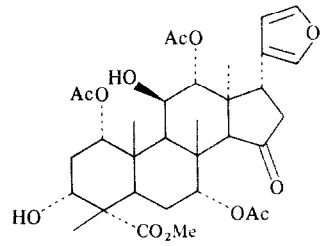

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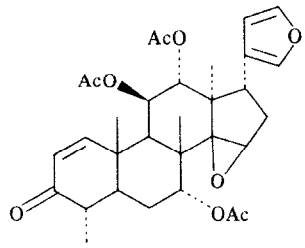

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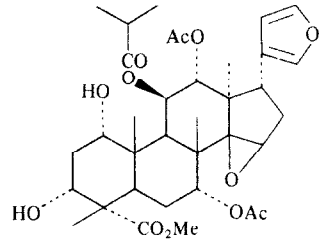
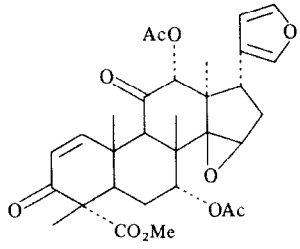


4 1-Acetate
5 3-Acetate



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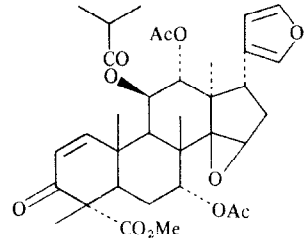

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Hydrolysis of the oxidation product of compound **B** was accompanied by decarboxylation, and reacetylation gave a crystalline product **3**, having a secondary methyl group. The formation of this compound proves the location of the methoxycarbonyl at C-4, and the location of the glycol grouping at C-11,C-12, instead of C-6,C-7; since H-9 is still visible as a doublet (δ2.95, J = 5 Hz; H-4, *dq*, J = 7, 3 Hz) and supports the sterochemistry assigned at C-4, the isomeric axial methoxycarbonyl would not have been expected to hydrolyse so easily. Failure to obtain a similar product from compound **A** is due to the fact that the oxidation product has a keto group at C-11, and therefore with alkali undergoes isomerization, leading to an intractable mixture of 11,12-ketols.

The third compound, **C**, $C_{37}H_{50}O_{13}$, was isomeric with **B** and had very similar spectral properties. It is an obvious suggestion that it is the corresponding 1-hydroxy-3-acetoxy compound, analogous to the known havanensin acetates. Oxidation gave a dehydro derivative in which H-11 is strongly shifted downfield by the effect of the new C-1 keto group, and the mass spectrum shows a prominent $[M-60]^+$ peak, due to the loss of the 3-acetate. These facts support the proposal. The oxidation produces no shift of any of the acetate ^{1}H NMR resonances, which is in agreement with the suggestion that the isobutyryl ester is at C-11. We therefore propose structures **4** and **5** respectively for compounds **B** and **C**.

These compounds are very similar to havanensin, heudelottin and hirtin, which are typical limonoids of the genus *Trichilia* [7], representing intermediates or byways on the route to the more characteristic prieurianin group. They are consistent with the occurrence of prieurianin in *Turraea obtusifolia*, and with the close taxonomic relationship of *Turraea* and *Nymania*.

EXPERIMENTAL

Extraction. The bark of *Turraea floribunda* was ground and extracted with refluxing *iso*-hexane, yielding a gum (30 g). Chromatography of this on alumina yielded a fraction (1.5 g) which was rechromatographed on prep. TLC plates.

Compound **A** (268 mg) had mp 251–252°. (Found: C, 62.34; H, 7.34; *m/z* 632. $C_{33}H_{44}O_{12}$, requires: C, 62.65; H, 6.96%; *m/z* 632.) ^{13}C NMR: δ175.3 (*s*), 173.3 (*s*), 170.2 (*s*), 169.5 (*s*), 142.4 (*d*), 140.6 (*d*), 128.3 (*s*), 112.4 (*d*), 87.3 (*d*), 74.6 (*d*), 74.3 (*d*), 74.0 (*d*), 74.0 (*s*), 73.4 (*d*), 63.2 (*d*), 53.5 (*q*), 51.5 (*s*), 48.0 (*s*), 41.4 (*d*), 41.2 (*d*), 41.2 (*d*), 41.0 (*s*), 40.1 (*s*), 32.5 (*t*), 32.2 (*d*), 27.8 (*t*), 25.5 (*t*), 24.0 (*q*), 21.4 (*q*), 21.4 (*q*), 20.9 (*q*), 18.3 (*q*), 16.8 (*q*), 16.8 (*q*). ^{1}H NMR: δ7.26, 7.13 (*m*, H-21, 23), 6.43 (*m*, H-22), 5.12 (*m*, $W_{1/2}$ = 5 Hz, H-1), 4.65 (*m*, $W_{1/2}$ = 5 Hz, H-7), 4.36 (*d*, J = 3 Hz, H-12), 3.75 (2H, *m*, H-3, 11), 3.65 (3H, *s*, CO_2Me), 3.60 (*s*, H-15), 3.00 (*m*, H-9), 2.13, 2.12, 2.05 (3 × Ac), 1.4, 1.32, 1.20, 1.0 (4 × CMe). The acetate had mp 290–291°. (Found: C, 62.13; H, 6.49; *m/z* 716. $C_{37}H_{48}O_{14}$, requries: C, 62.01; H, 6.7%; *m/z* 716.) ^{13}C NMR: δ173.8 (*s*), 170.9

(*s*), 170.0 (*s*), 169.6 (*s*), 169.3 (*s*), 169.0 (*s*), 142.4 (*d*), 140.7 (*d*), 128.1 (*s*), 112.4 (*d*), 79.6 (*d*), 74.4 (*d*), 74.0 (*d*), 74.0 (*s*), 73.3 (*d*), 72.3 (*d*), 63.2 (*d*), 52.0 (*q*), 49.6 (*s*), 48.7 (*s*), 40.6 (*s*), 40.4 (*d*), 40.3 (*s*), 40.3 (*d*), 33.3 (*t*), 32.6 (*t*), 25.2 (*t*), 24.6 (*t*), 23.7 (*q*), 21.5 (*q*), 21.3 (*q*), 21.2 (*q*), 20.9 (*q*), 20.9 (*q*), 17.8 (*q*), 17.0 (*q*), 16.8 (*q*). ^{1}H NMR: δ7.26, 7.08 (*m*, H-21, 23), 6.40 (*m*, H-22), 5.20 (*m*, H-11), 4.97 (*m*, $W_{1/2}$ = 5 Hz, H-1), 4.88 (*d*, *J* = 3 Hz, H-12), 4.65 (2H, *m*, H-3, H-7), 3.60 (*s*, H-15), 3.55 (3H, *s*, CO_2Me), 3.38 (*d*, *J* = 3 Hz, H-9), 2.13, 2.10, 2.10, 2.03, 1.90 (5 × Ac), 1.30, 1.20, 1.16, 1.03 (4 × CMe).

Compound **B** had mp 233–234°. (Found: C, 63.06; H, 7.6; *m/z* 702. $C_{37}H_{50}O_{13}$ requires: C, 63.23; H, 7.17%; *m/z* 702.) ^{13}C NMR: δ176.4 (*s*), 175.2 (*s*), 170.1 (*s*), 169.3 (*s*), 168.8 (*s*), 142.5 (*d*), 140.6 (*d*), 128.1 (*s*), 112.3 (*d*), 79.2 (*d*), 74.2 (*d*), 74.2 (*d*), 74.0 (*d*), 73.8 (*s*), 73.2 (*s*), 63.3 (*d*), 52.0 (*q*), 51.5 (*s*), 48.9 (*s*), 40.7 (*s*), 40.7 (*d*), 40.2 (*s*), 40.2 (*d*), 34.3 (*d*), 32.5 (*d*), 32.5 (*t*), 27.1 (*t*), 25.4 (*t*), 23.8 (*q*), 21.4 (*q*), 21.4 (*q*), 19.0 (*q*), 18.8 (*q*), 17.7 (*q*), 16.7 (*q*), 16.7 (*q*). ^{1}H NMR: δ7.23, 7.03 (*m*, H-21, 23); 6.38 (*m*, H-22), 5.15 (*m*, H-11), 4.86 (*m*, H-1), 4.68 (*d*, $W_{1/2}$ = 5 Hz, H-12), 4.68 (*m*, *J* = 3 Hz, H-7), 3.75 (*br s*, H-3), 3.63 (*s*, 4H, H-15, CO_2Me), 3.63 (*d*, *J* = 3 Hz, H-9), 2.12, 2.10, 2.02 (3 × Ac), 1.30, 1.21 (2 × CMe), 1.18, 1.16 (*d*, *J* = 7 Hz, 2 × CHMe), 1.15, 1.02 (2 × CMe). The acetate had mp 214–215°. (Found: C, 62.72; H, 6.78; *m/z* 744. $C_{39}H_{52}O_{14}$ requires: C, 62.89; H, 7.04%; *m/z* 744.) ^{13}C NMR: δ176.4 (*s*), 173.8 (*s*), 170.0 (*s*), 169.4 (*s*), 169.1 (*s*), 169.1 (*s*), 142.4 (*d*), 140.6 (*d*), 128.2 (*s*), 112.4 (*d*), 79.2 (*d*), 74.3 (*d*), 74.1 (*d*), 74.0 (*s*), 73.3 (*d*), 72.3 (*d*), 63.3 (*d*), 49.6 (*s*), 49.0 (*s*), 40.4 (*s*), 40.4 (*d*), 40.1 (*s*), 40.1 (*d*), 34.3 (*d*), 33.3 (*d*), 32.6 (*t*), 25.2 (*t*), 24.6 (*t*), 23.7 (*q*), 21.4 (*q*), 21.4 (*q*), 21.4 (*q*), 21.2 (*q*), 20.9 (*q*), 19.0 (*q*), 18.8 (*q*), 17.8 (*q*), 17.0 (*q*), 16.6 (*q*). ^{1}H NMR: δ7.26, 7.08 (*H*-21, 23), 6.40 (*m*, H-22), 5.20 (*m*, H-11), 4.98 (*m*, $W_{1/2}$ = 5 Hz, H-1), 4.88 (*d*, *J* = 3 Hz, H-12), 4.66 (*br s*, H-3), 4.66, (*m*, H-7), 3.60 (*s*, H-15), 3.56 (3H, *s*, CO_2Me), 3.39 (*d*, *J* = 3 Hz, H-9), 2.15, 2.08, 2.05, 1.92 (4 × Ac), 1.32, 1.23 (2 × CMe); 1.20, 1.16 (*d*, *J* = 7 Hz, 2 × CHMe), 1.18, 1.08 (2 × CMe).

Compound **C** (180 mg) was obtained from prep. TLC of another fraction. It remained amorphous. ^{13}C NMR: δ176.9 (*s*), 173.8 (*s*), 170.2 (*s*), 170.0 (*s*), 168.5 (*s*), 142.3 (*d*), 140.5 (*d*), 128.3 (*s*), 112.4 (*d*), 79.2 (*d*), 75.2 (*d*), 74.9 (*d*), 74.5 (*s*), 74.0 (*d*), 70.4 (*d*), 63.1 (*d*), 52.0 (*q*), 49.8 (*s*), 49.0 (*d*), 42.0 (*s*), 40.9 (*d*), 40.0 (*s*), 39.6 (*d*), 34.3 (*d*), 32.6 (*t*), 32.1 (*d*), 27.8 (*t*), 25.2 (*t*), 23.7 (*q*), 21.7 (*q*), 21.4 (*q*), 21.0 (*q*), 19.2 (*q*), 18.6 (*q*), 18.1, (*q*), 16.6 (*q*), 16.2 (*q*). ^{1}H NMR: δ7.25, 7.05, (*m*, H-21, 23), 6.38 (*m*, H-22), 5.77 (*m*, H-11), 5.12 (*m*, H-3), 4.95 (*d*, *J* = 3 Hz, H-12), 4.65 (*m*, H-7), 3.60 (*s*, H-15), 3.53 (3H, *s*, CO_2Me), 3.45 (*d*, *J* = 4.5 Hz, H-9), 2.10, 2.00, 1.97 (3 × Ac), 1.29, 1.13, 1.19, 1.19 (4 × CMe), 1.10, 1.03 (2 × CHMe). Acetylation of the more polar fractions from the first chromatography gave a further amount of compound **A** acetate.

Oxidation of compound **A**. Compound **A** (60 mg) in DMF (1 ml) was oxidized with pyridinium dichromate (238 mg). Purification by TLC gave the dehydro compound **6**, (33 mg), mp 204–205°. (Found: C, 65.2; H, 6.45; *m/z* 568. $C_{31}H_{36}O_{10}$, requires: C, 65.48; H, 6.38%; *m/z* 568.) ^{13}C NMR: δ204.1 (*s*), 196.9 (*s*), 172.5 (*s*), 170.4 (*s*), 169.4 (*s*), 159.6 (*d*), 142.9 (*d*), 140.4 (*d*), 127.0 (*s*), 125.0 (*d*), 111.7 (*d*), 77.9 (*d*), 74.9 (*s*), 71.3 (*d*), 63.2 (*d*), 58.3 (*s*), 54.7 (*d*), 52.0 (*q*), 48.6 (*s*), 42.6 (*s*), 42.0 (*s*), 40.8 (*s*), 38.9 (*s*), 33.6 (*t*), 25.3 (*q*), 24.7 (*t*), 21.4 (*q*), 21.1 (*q*), 20.5 (*q*), 16.5 (*q*), 16.5 (*q*). ^{1}H NMR: δ7.82 (*d*, *J* = 10 Hz, H-1), 7.26, 7.10 (*m*, H-21, 23), 6.30 (*m*, H-22), 5.92 (*d*, *J* = 10 Hz, H-2), 5.32 (*s*, H-12), 4.72 (*m*, H-3), 3.56 (3H, *s*, CO_2Me), 3.62 (*s*, H-15), 3.56 (*s*, H-9), 2.22, 2.08 (2 × Ac), 1.40, 1.35, 1.30, 1.00 (4 × CMe).

Oxidation of compound **B**. Compound **B** (60 mg) in DMF (1 ml) was oxidized with pyridinium dichromate (360 mg). Purification by TLC gave the unsaturated ketone **7**, mp 209–210°. (Found: C, 65.72; H, 6.98; *m/z* 640. $C_{35}H_{44}O_{11}$ requires: C, 65.61; H, 6.92%; *m/z* 640.) ^{13}C NMR: δ197.2 (*s*), 176.7 (*s*), 172.5 (*s*), 170.2 (*s*), 169.5 (*s*), 156.3 (*d*), 142.6 (*d*), 140.5 (*d*), 128.0 (*s*), 125.5 (*d*), 112.1 (*d*), 78.4 (*d*), 74.3 (*s*), 73.4 (*d*), 73.1 (*d*), 63.4 (*d*), 58.1 (*s*), 52.0 (*q*), 48.9 (*s*), 43.8 (*s*), 43.8 (*d*), 40.9 (*s*), 39.8 (*s*), 39.8 (*d*), 34.3 (*d*), 32.7 (*t*), 25.2 (*q*), 24.0 (*t*), 21.5 (*q*), 21.1 (*q*), 21.1 (*q*), 19.2 (*q*), 18.6 (*q*), 16.7 (*q*), 16.3 (*q*). ^{1}H NMR: δ7.30 (*d*, *J* = 10 Hz, H-1), 7.25, 7.06 (*m*, H-21, 23), 6.35 (*m*, H-22), 5.95 (*d*, *J* = 10 Hz, H-2), 5.88 (*m*, H-11), 5.06 (*d*, *J* = 3 Hz, H-12), 4.68 (*m*, H-7), 3.65 (3H, *s*, CO_2Me), 3.61 (*s*, H-15), 2.96 (*d*, *J* = 3 Hz, H-9), 2.10, 2.02 (2 × Ac), 1.41, 1.35, 1.31 (3 × CMe), 1.26, 1.16 (*d*, *J* = 7 Hz, CHMe), 0.95 (CMe).

Oxidation of compound **C**. Compound **C** (60 mg) was oxidized as described above, the product remained amorphous. (Found: *m/z* 700.3091; $C_{37}H_{48}O_{13}$ requires: *m/z* 700.3095.) ^{13}C NMR: δ209.4 (*s*), 176.9 (*s*), 173.4 (*s*), 169.9 (*s*), 169.4 (*s*), 169.1 (*s*), 142.4 (*d*), 140.5 (*d*), 128.2 (*s*), 112.3 (*d*), 78.7 (*d*), 74.1 (*s*), 73.0 (*d*), 63.3 (*d*), 52.3 (*q*), 50.7 (*s*), 50.0 (*s*), 48.8 (*s*), 41.6 (*d*), 41.0 (*d*), 40.7 (*d*), 40.1 (*s*), 39.9 (*d*), 39.7 (*t*), 34.3 (*d*), 32.8 (*t*), 24.8 (*t*), 24.3 (*q*), 21.5 (*q*), 21.2 (*q*), 20.8 (*q*), 19.2 (*q*), 18.6 (*q*), 17.7 (*q*), 17.1 (*q*), 16.5 (*q*). ^{1}H NMR: δ7.27, 7.08 (*m*, H-21, 23), 6.38 (*m*, H-22), 5.25 (*m*, H-3), 5.25 (*m*, H-11), 4.67 (*m*, H-7), 5.00 (*d*, *J* = 3 Hz, H-12), 3.65 (3H, *s*, CO_2Me), 3.60 (*s*, H-15), 3.00 (*d*, *J* = 3 Hz, H-9), 2.10, 2.08, 1.98 (3 × Ac), 1.50, 1.40, 1.35, 1.05 (3 × CMe), 1.26, 1.20 (2 × CHMe), 1.05 (CMe).

Alkaline hydrolysis of **7**. The enone **7** (50 mg) was refluxed with ethanolic KOH (25 ml, 1.2%) for 1.5 hr. Purification by TLC gave, after acetylation, the decarboxylated compound (28 mg), mp 135–136°. (Found: C, 66.82; H, 7.18; *m/z* 554.2511. $C_{31}H_{38}O_9$ requres: C, 67.13; H, 6.91; *m/z* 554.2515.) ^{1}H NMR: δ7.27 (*d*, *J* = 10 Hz, H-1), 7.33, 7.14 (*m*, H-21, 23), 6.40 (*m*, H-22), 5.92 (*d*, *J* = 10 Hz, H-2), 5.94 (*m*, H-11), 5.12 (*d*, *J* = 3 Hz, H-12), 4.77 (*m*, H-7), 4.17 (*dq*, *J* = 3, 7 Hz, H-4), 3.68 (*s*, H-15), 2.95 (*d*, *J* = 5 Hz, H-9), 2.17, 2.15, 2.09 (3 × Ac), 1.41, 1.40, 0.98 (3 × CMe), 1.08 (*d*, *J* = 7 Hz, CHMe).

Acid rearrangement of compound **A**. Compound **A** (100 mg) in methanolic HCl (80 ml, 0.5 N) was refluxed 1 hr. Purification by TLC gave the rearranged ketone (18 mg). (Found: *m/z* 632.2829. $C_{33}H_{44}O_{12}$ requires *m/z* 632.2832.) ^{1}H NMR: δ7.26, 7.13 (*m*, H-21, 23), 6.43 (*m*, H-22), 5.16 (*m*, H-1), 4.60 (*m*, H-7), 4.43 (*m*, H-11, H-12), 3.85 (*m*, H-3), 3.55 (3H, *s*, CO_2Me), 3.20 (*d*, *J* = 3 Hz, H-9), 2.18, 2.10, 2.00 (3 × Ac), 1.38, 1.33, 1.23, 1.03 (4 × CMe).

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