GNETINS: RESVERATROL OLIGOMERS FROM *GNETUM* SPECIES[1]

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ABSTRACT.—*Gnetum leyboldii* and *G. schwackeanum* (Gnetaceae) are lianas of Amazonia. The former contains in its wood the gnetins A,B,C,D and E for which the structures of *rel*-(1R,5R,6R,7R)-6-(4-hydroxyphenyl)-7-(3,5-dihydroxyphenyl)-2-(E) - (4-hydroxystyryl) - 4,8-dioxobicyclo | 3.2.1 | oct-2-ene; 1-hydroxy-5-(4-hydroxyphenyl)-6-(3,5-dihydroxyphenyl)-3-(E)-(4-hydroxystyryl)-7-oxobicyclo|2.2.2|oct-2-ene; *rel*-(2S, 3S)-4-hydroxy-2-(4-hydroxyphenyl)-3- (3,5-dihydroxyphenyl)-6-(E)-(4-hydroxystyryl)-2,3-dihydrobenzofuran; *rel*-(2S,3S)-4-hydroxy-2-(2,4-dihydroxyphenyl)-3-(3,5-dihydroxyphenyl)-6-(E)-(4-hydroxystyryl)-2,3-dihydrobenzofuran; and *rel*-(2S,3S)-4-hydroxy-2-(4-hydroxyphenyl)-3-[6-*rel*-(2S,3S)-4-hydroxy-2-(4-hydroxyphenyl)-3-(3,5-dihydroxyphenyl)-2,3-dihydrobenzofuranyl]-6-(E)-(4-hydroxystyryl)-2,3-dihydrobenzofuran were proposed, respectively. The fruits of *G. schwackeanum* contain the gnetins C and E.

Of the 33 recognized *Gnetum* species, only 6 occur in tropical America, *G. leyboldii* Tull. being distributed towards the south of Amazonia mainly in marshy or periodically flooded regions and *G. schwackeanum* Taub. occurring throughout the State of Amazonas on "terra firme" (non-flooded ground) (2). An ethanol extract of the woody part of the former liana contained five novel compounds designated gnetins A to E. An acetone extract of the fruits of the latter liana contained the gnetins C and E.

RESULTS

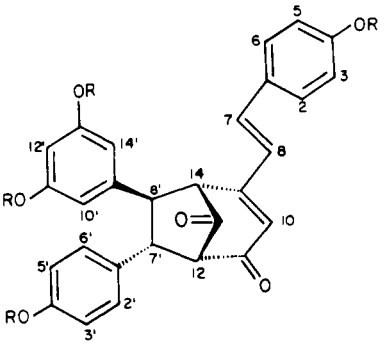
The constitution and relative configuration **1a** for gnetin-A was deduced as follows. The compound, $C_{28}H_{22}O_6$, gave a tetrahydroderivative, $C_{28}H_{26}O_6$ (**1b**), and a tetraacetate, $C_{28}H_{18}O_2$ $(OAc)_4$ (**1c**). The two undefined oxygens are part of an α,β-unconjugated ketone (νmax 1670 cm^{-1}) and of a cyclopentanone (νmax 1760 cm^{-1}). Comparison of the ^1H nmr spectra of gnetin-A and of its tetraacetate revealed the location of the four hydroxyls on two 4-hydroxyphenyl and one 3,5-dihydroxyphenyl groups (table 1). Hydrogenation of gnetin-A produced only one significant nmr spectral modification related to aromatic protons. The AA'-signal representing H-2 and H-6 of one of the 4-hydroxyphenyl groups shifted from δ 7.56 to δ 7.24; the group was, thus, part of a styryl system. The intense uv absorption of gnetin-A suggested the conjugation of the styryl portion to be extended by the α,β-unsaturated ketone moiety. Indeed, the observed data (λmax 367 nm, ϵ=25900) are compatible with the expected data (λmax ca. 377 nm, ϵ=ca. 45000) (3) for such a δ-(4-hydroxyphenyl)-$\alpha,\beta,\gamma,\delta$-unsaturated ketone system. Neither the *trans* CH=CH group, evidenced by two doublets (δ 7.15 and 7.28, J=16Hz), nor H-α, evidenced by a broad singlet (δ 6.26), of this system showed further vicinal couplings. For this reason substitution must occur at the β-carbon and at the carbonyl, as shown in **1a**.

[1]Part I of the proposed series "The chemistry of Brazilian Gnetaceae. For a preliminary report on gnetin-A see Ref. (1).

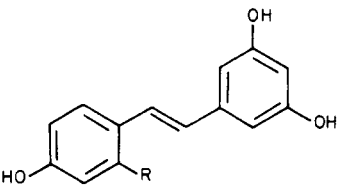
TABLE 1. ^{1}H nmr data of resveratrol oligomers.

	1a		**3**		**4a**		**4b**		**5** |9|		**6** |10|		**7a**	
	δ mul.	*J*	δ mul.	*J*	δ mul.	*J*	δ mul.	*J*	δ mul.	*J*	δ mul.	*J*	δ mul.	*J*
2 }	7.56 d	8.5	7.38 d	8.5	7.45 d	8.5	7.45 d	8.5	7.22 d	8.5	7.26 bs	8.5	}7.44 d	8.5
6 }											7.40 dd	8.5		
												1.5		
3 }	6.88 d	8.5	6.82 d	8.5	6.85 d	8.5	6.85 d	8.5	6.86 d	8.5	—		}6.85 d	8.5
5 }											6.86 d	8.5		
7	7.28 d	16.0	6.91 d	16.5	7.11 d	16.5	7.12 d	16.5	6.93 d	16.0	7.06 d	16.5	7.11 d	16.5
8	7.15 d	16.0	6.76 d	16.5	6.97 d	16.5	6.97 d	16.5	6.73 d	16.0	6.88 d	16.5	6.97 d	16.5
10	6.26 t	1.0	6.19 s		6.60 bd	1.0	6.57 bd	1.0	—		6.55 d	2.0	6.63 bs	
12	3.68 ddd	7.0	3.83 d	14.0	—		—		6.35 d	2.1	6.28		—	
		1.5												
		1.0	3.15											
14	3.87 dd	1.5	3.02		6.70 bd	1.0	6.73 bd	1.0	6.75 d	2.1	6.55 d	2.0	6.72 bs	
		1.0												
2' }	7.09 d	8.5	6.92 d	8.5	7.22 d	8.5	—		}7.17 d	8.5	7.22 d	8.7	}7.25 d	8.5
6' }							7.02 d	8.5						
3' }	6.74 d	8.5	6.65 d	8.5	6.84 d	8.5	6.46 d	2.5	}6.76 d	8.5	6.84 d	8.7	6.86 d	8.5
5' }							6.29 dd	8.5						
								2.5						
7'	3.77 t	7.0	3.15		5.39 d	4.5	5.74 d	3.5	5.45 d	5.4	5.46 d	8.0	5.48 d	4.5
8'	3.43 d	7.0	3.02 d	5.5	4.39 d	4.5	4.43 d	3.5	4.50 d	5.4	4.44 d	8.0	4.48 d	4.5
10' }	6.19 d	2.0	6.14 d	2.0	6.17 d	2.0	6.26 d	2.0			}6.20 d	2.2	6.24 bs	
14' }									}6.27 s				6.32 bs	
12'	6.26 t	2.0	6.12 t	2.0	6.24 t	2.0	6.21 t	2.0			6.28		—	
2",6"													7.20 d	8.5
3",5"													6.84 d	8.5
7"													5.38 d	5.5
8"													4.39 d	5.5
10",14"													6.18 d	2.0
12"													6.24 t	2.0

^{1}Chemical shifts (δ) in ppm from internal TMS for $(CD_3)_2CO$ solutions at 270 MHz (**1a, 3, 4a, 4b, 7a**) and 100 MHz (**5,6**); coupling constants (*J*) in Hz; s singlet, d doublet, dd double doublet, ddd double double doublet, t triplet, b broad.



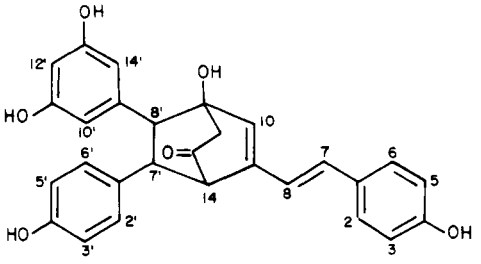
1a R=H
1b R=H, 7,8,9,10-tetrahydro
1c R=Ac



2a R=H
2b R=OH

The foregoing deductions accounted for 17 sp^2-carbon signals of the ^{13}C nmr spectrum representing 23 carbons, and only one sp^2-carbon signal and four sp^3-carbon signals remained to be assigned. These five signals indicated the cyclopentanone moiety to include, besides the carbonyl (δ 203.6, singlet), four methines (δ 72.8, 56.4, 54.2 and 51.7, all doublets).

The four moieties (two aryls, one δ-aryl-$\alpha,\beta,\gamma,\delta$-unsaturated ketone and one cyclopentanone) fit into a structure, formally derived by dehydrodimerization of resveratrol (**2a**), such as **1a**. Indeed, **1a** would explain the relatively large chemical shift of one of the methine carbons (δ 72.8) in view of the location of C-12 on a bridgehead between two carbonyls (4), as well as the W-couplings between H-14 and H-10 (J=1.0Hz), H-10 and H-12 (J=1.0Hz) and H-12 and



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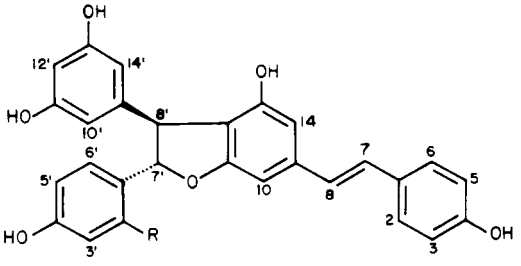
H-14 (J=1.5Hz) in view of the location of the three protons at alternate positions of a hexacycle. The assignments of the H-14 (δ 3.87) and H-12 (δ 3.68) resonances were based on the recognition of the allylic nature of H-14. In contrast to the signal of H-12, the H-14 signal was strongly shifted upfield (to δ 2.70) upon hydrogenation. In another contrasting feature, H-14 showed no additional coupling, a fact which established the $H^{14}C.CH^{8'}$ dihedral angle at about 90°. Vicinal couplings, however, occurred between H-12 and H-7', (δ 3.77, triplet, J=7.0Hz), as well as between H-7' and H-8' (δ 3.43, doublet, J=7.0Hz). In consequence, the bicyclo (3.2.1) octane skeleton of gnetin-A must be substituted

by 7'-*endo* and 8'-*exo*-aryls. Double irradiation at the frequency of H–7' not only collapsed the H–12 double doublet into a broad singlet and the H–8' doublet into a singlet but also produced a 10% intensity enhancement of the H–2', H–6' signal of the unconjugated 4-hydroxyphenyl. This must, hence, occupy position 7'. The *ortho* proton signals of both of the other aryls were unaffected, and the 3,5-dihydroxyphenyl group can only occupy position 8'. All other possible double irradiation experiments were performed, and the observed band simplifications and Overhauser-effects were fully consistent with the proposed structure **1a**.

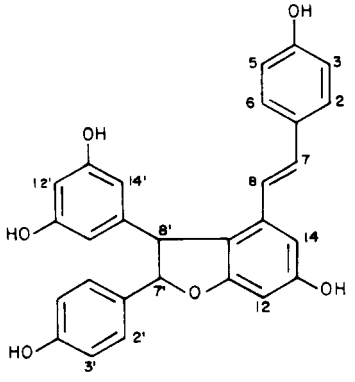
Comparison of ^{1}H nmr data with **1a** (gnetin-A) (table 1) suggested constitution **3** for gnetin-B, $C_{28}H_{24}O_6$. Indeed, a 4-hydroxyphenyl and a 3,5-dihydroxyphenyl group, both linked to sp^3-carbons, were again represented by comparable signals (table 1). The H–7, 8 and 10 signals of the 4–OH–C_6H_4·CH=CH·C=CH moiety all appeared at somewhat higher field, indicating the absence of a conjugated carbonyl in **3**. Accordingly, the α,β-unsaturated ketone band was absent from the ir spectrum of **3**, as was the cyclopentanone band, here replaced by a cyclohexanone band (1740 cm^{-1}). Accomodation of these structural units, as shown in the bicyclo (2.2.2) octanoid formula **3**, is not only consistent with all the spectral evidence but also conforms again to a biosynthetic process involving the dimerization of resveratrol (**2a**).

Gnetin-C (**4a**) possesses the molecular formula $C_{28}H_{22}O_6$ and is thus, isomeric



4a R=H
4b R=OH

with gnetin-A (**1a**). Analysis of its ^{1}H nmr spectrum (table 1) showed, again, substitution of a $C_8H_5O_2$ core by 4-hydroxystyryl, 4-hydroxyphenyl and 3,5-dihydroxyphenyl units. Here, however, the central group was formed by a dihydrobenzofuran unit precisely as in ϵ-viniferin (**5**), a phytoalexin from *Vitis vinifera* (5). Although these units have two meta-related protons on resorcinol-



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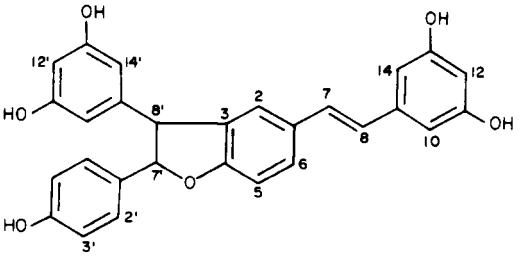

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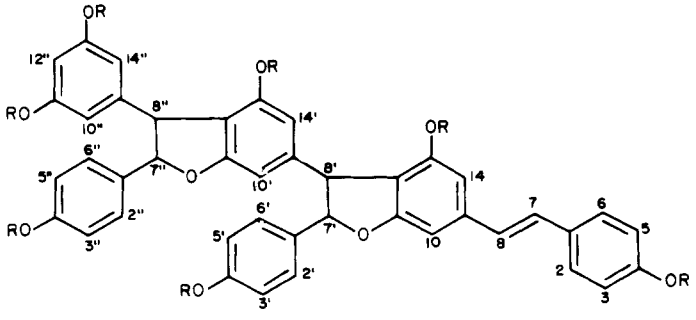
type aromatic rings in both, **4a** and **5**, the environment of the protons is different. While in **4a** H–10 (δ 6.60, d, $J=1$Hz) and H–14 (δ 6.70, d, $J=1$Hz) are both vicinal to the styryl substituent, in **5** not H–12 (δ 6.35, d, $J=2.1$ Hz) but only H–14 (δ 6.75, d, $J=2.1$Hz) is vicinal to the deshielding group. Still another isomer of gnetin-C, the dehydrodimer **6** obtained by treatment of resveratrol (**2a**) with horseradish-hydrogen peroxide (6), serves as a good model, although the two aromatic rings linked to the vinyl group are interchanged. Here, as in **4a**, H–10 and H–14 (δ 6.55, d, $J=2$Hz) are *ortho*-related to the styryl substituent and are again considerably less shielded than the *para*-related H–12 (δ 6.28). The location of the styryl group in **4a** was confirmed by double irradiation of H–8 (δ 6.97), which not only produced an Overhauser-effect on H–2 and H–6 (at δ 7.45) but also improved the resolution of both broad doublets corresponding to H–10 and H–14 (at δ 6.60 and 6.70). The relative location of the two aryls on the hydrobenzofuran system was established by the observation of enhancement of intensity of the H–2', H–6' signal (at δ 7.22) upon double irradiation of H–7 and *vice versa* (due to nuclear Overhauser-effect and/or elimination of benzylic coupling).

All differences in the ^{1}H nmr spectra of gnetin-C (**4a**, $C_{28}H_{22}O_6$) and gnetin-D (**4b**, $C_{28}H_{22}O_7$) are accounted for by the additional presence of a hydroxyl at C–2' of the latter compound. Indeed, upon comparison of the spectra of **4a** and **4b** (table 1), significant shifts were observed only for the resonances due to H–3', H–5', H–6' and H–7' ($\Delta\delta$ resp. -0.38, -0.55, -0.20, $+0.35$). The strong deshielding of H–7' must be attributed to the existence of a hydrogen-bridge between the OH at C–2' and the heterocyclic oxygen, thus confirming the location of the 2,4-dihydroxyphenyl group at C–7'. Again, as in **4a**, in **4b** the 4-hydroxystyryl is vicinal to two unsubstituted aryl positions, since double irradiation of H–8 (at δ 6.97) affected both originally broad doublets due to H–10 and H–14 (at δ 6.57 and 6.73). In gnetin-D (**4b**) two different stilbenes, resveratrol (**2a**) and oxyresveratrol (**2b**) are oxidatively associated.

Although the 270 MHz ^{1}H nmr spectrum of gnetin-E is quite complex, its peaks are easily assigned to the protons of **7a** upon the assumption that the differences of the resonances of gnetin-C and the outermost stilbene portions of gnetin-E are smaller ($\Delta\delta$ 0.00 ± 0.01) than the differences of the resonances of gnetin-C and the innermost stilbene portion of gnetin-E ($\Delta\delta$ 0.08 ± 0.09). All possible double irradiation experiments were performed and, together with the spectral shifts observed upon acetylation to the heptaacetate (**7b**), confirmed the structure as the *trans, trans*-form of (**7a**), an oxidative trimer of resveratrol (**2a**).

We have postulated, so far, a *trans* relationship between the two aryl groups that substitute the dihydrofuran ring. This is the most common configuration

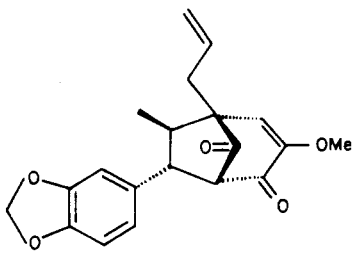


7a R=H
7b R=Ac

for this type of products in nature (6), but it cannot be easily substantiated by ^{1}H nmr vicinal coupling constants (7) since conformational factors influence quite strongly the dihedral angles involving C–7', C–8' and C–7", C–8". *A priori* it could be postulated that this angle should be substantially identical in all dihydrobenzofurans mentioned in the paper (**4a**, **4b**, **5**, **6**, **7a**, **7b**). That this is not the case is clearly due to differential substitution at the *ortho*-positions of aromatic rings. The presence of a hydroxyl at this position is especially efficient in depressing the *J* H–7', H–8' value. This is, in Hz, 8.0 in **6** (with H–2) and 8.5/7.5 in **7b** (with resp. OAc-15'/OAc-15) against only 5.5/4.5 in **7a** (with resp. OH–15'/OH–15) and 4.5 in **4a** (with OH–15), and even as low as 3.5 in **4b** (with OH–15 and OH–2'). A *para* hydroxystyryl group at C–15 (**5**) also diminishes *J* H–7', H–8' (to 5.4 Hz), albeit somewhat less strongly than a hydroxyl. A *posteriori* such facts can be used diagnostically, e.g., in the distinction of gnetin C (**4a**) from ε-viniferin (**5**) and in the assignment of ^{1}H resonances to the outermost *versus* the inner dihydrobenzofuran portions of oxidative resveratrol trimers, tetramers etc. of type **7a**.

DISCUSSION

Resveratrol (**2a**) occurs in gymnosperms (Pinaceae) as well as in angiosperms (Leguminosae [Fabaceae], Myrtaceae, Vitaceae, Moraceae and Liliaceae), being accompanied in the latter two families by oxyresveratrol (**2b**). The bicyclo-octanoid dimers gnetins-A (**1a**) and B (**3**) belong to novel natural product types. Dihydrobenzofuranoid oligomers, albeit of different structures than gnetins-C (**4a**), D (**4b**) and E (**7**), are constituents of Dipterocarpaceae and phytoalexins of Vitaceae (8).



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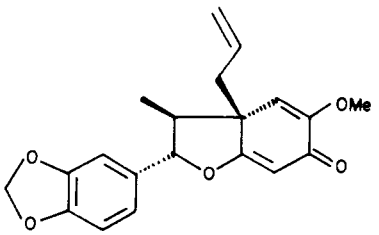
The most notable feature of the present findings is the structural analogy of gnetins with the oxidative dimers of propenylphenols and allyphenols, e.g. **8**, **9** and **10** (9). Such bicyclo (3.2.1) octanoid and hydrobenzofuranoid neolignans are chemically interconvertible, e.g., **8**→**9** (10). An analogous rearrangement may conceivably also operate in the gnetin series.



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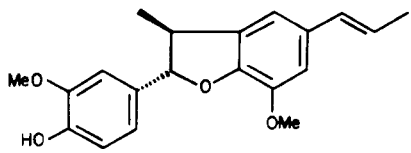

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EXPERIMENTAL

ISOLATION OF THE CONSTITUENTS OF *Gnetum leyboldii*.—The liana was collected at the shores of the Guamá River, Pará State. A sample of dry, powdered bark (450 g) was extracted successively with light petroleum ether, ethyl acetate and ethanol. The ethanol was evaporated. To the residue (15 g) in methanol (30 ml) chloroform was added. The precipitate was filtered and mixed with Si gel. The powder was introduced on top of a Si gel (600 g) column. Elution with chloroform gave aliphatic material (2.5 g). Elution with chloroform-ethyl acetate (7:3) gave a solid (7 g) which was fractionated by preparative tlc [Si gel, chloroform-methanol (9:1)] into a less polar part A and a more polar one B. Part A was separated by repeated tlc [Si gel, chloroform-methanol (9:1)] into **4a** (40mg), **1a** (1g), and **3** (30mg). Part B was separated by repeated tlc [Si gel, chloroform-methanol (8:2)] into **7a** (200mg) and **4b** (30mg).

ISOLATION OF THE CONSTITUENTS OF *Gnetum schwackeanum*.—The liana was collected in the Biological Reserve of INPA, km 45 of the Manaus-Caracaraí road. The peeled, ground fruits (100g) were percolated with ethanol. The extract (2 g) was washed successively with light petroleum ether, chloroform and acetone. The chloroform soluble part (1 g) was chromatographed on Si gel (100 g). Elution (100 ml fractions) was performed with chloroform-methanol (95:5) (frs. 1–60), 85:15 (frs. 80–90, 91–100), 80:20 (frs. 101–106, 107–117). Purification of frs. 80–90 and 101–106 by preparative tlc (Si gel, ether) gave respectively **4a** (100 mg) and **7a** (200 mg).

Gnetin-A (**1a**), yellow crystals, mp 179–180° (purified by tlc). Found: C, 73.69, H, 4.94; $C_{28}H_{22}O_6$ requires: C, 74.00, H, 4.88%; ν max (KBr) cm^{-1}: 3450, 1760, 1670, 1600, 1530, 1500, 1480, 1360, 1010, 970, 840; λ max (MeOH) nm: 253 (ϵ 300), 278 (ϵ 250), 367 (ϵ 25900); ^{13}C nmr (22.6 MHz, $(CD_3)_2CO$) δ: 127.8 (s, C-1), 130.1 (d, C-2,6), 115.8 (d, C-3,5), 161.8 (s, C-4), 138.8 (d, C-7), 122.7 (d, C-8), 156.9 (s, C-9), 126.7 (d, C-10), 195.5 (s, C-11), 72.8 (d, C-12), 203.6 (s, C-13), 56.4 (d, C-14), 129.3 (s, C-1'), 130.3 (d, C-2', 6'), 116.4 (d, C-3', 5'), 159.3 (s, C-4'), 54.2 (d, C-7'), 51.7 (d, C-8'), 146.9 (s, C-9'), 105.5 (d, C-10', 14'), 159.7 (s, C-11', 13'), 102.1 (d, C-12'); ms *m/z* (rel. int.): 454 (7) $M^{+\cdot}$, 360 (5), 348 (2), 280 (2), 266 (2), 242 (2), 226 (2), 188 (2), 147 (3), 137 (6), 120 (6), 107 (25), 97 (10), 94 (56), 81 (39), 69 (81), 57 (53), 44 (100).

Tetrahydro-derivative (**1b**) (**1a**, H_2/Pd, MeOH), mp 124–127° (purified by tlc) ν max (KBr) cm^{-1}: 3400, 1740, 1690, 1570, 1480, 1420, 1340, 1130, 1000, 840; λ max (MeOH) nm: 225 (ϵ21800), 279 (ϵ5000); ^1H nmr (270 MHz, $(CD_3)_2CO$) δ: 7.24 (d, J=8.5, H-2,6), 6.78 (d, J=8.5, H-3,5), 2.58 (dd, J=8.0, 6.0, 2H-7), 2.0 (m, 2H-8, H-9), 2.49 (bdd, J=16.0, 6.0, 2H-10), 3.67 (ddd, J=6.5, 1.5, 1.0, H-12), 2.67 (dd, J=1.5, 1.0, H-14), 7.04 (dd, J=8.5, H-2', 6'), 6.74 (d, J=8.5, H-3', 5'), 3.81 (t, J=6.5, H-7'), 3.84 (d, J=6.5, H-8'), 6.36 (d, J=2.0, H-10', 14'), 6.24 (t, J=2.0, H-12'); ^{13}C nmr |22.6 MHz, $(CD_3)_2CO$| δ: 128.6 (s, C-1), 128.8 (d, C-2,6), 115.3 (d, C-3,5), 157.4 (s, C-4), 34.8 (t, C-7), 32.3 (t, C-8), 36.1 (d, C-9), 42.9 (t, C-10), 206.3 (s, C-11), 72.1 (d, C-12), 206.5 (s, C-13), 59.0 (d, C-14), 129.0 (s, C-1'), 129.5 (d, C-2', 6'), 115.6 (d, C-3', 5'), 155.9 (s, C-4'), 49.5 (d, C-7'), 43.1 (d, C-8'), 148.6 (s, C-9'), 105.9 (d, C-10', 14'), 156.7 (s, C-11', 13'), 101.6 (d, C-12').

Tetraacetate (**1c**) (**1a**, Ac_2O, C_5H_5N, room temp., 24hr.), mp 94–97° (purified by tlc). ν max (KBr) cm^{-1}: 1780, 1750, 1660, 1560, 1490, 1430, 1380, 1030, 910, 840, 750; ^1H nmr (270 MHz, $CDCl_3$) δ: 7.57 (d, J=8.5Hz, H-2,6), 7.13 (d, J=8.5Hz, H-3,5), 7.08 (d, J=16.0Hz, H-7), 7.05 (d, J=16.0Hz, H-8), 6.30 (t, J=1.0Hz, H-10), 3.84 (ddd, J=7.0, 1.5, 1.0Hz, H-12), 3.84 (dd J=1.5, 1.0Hz, H-14), 7.05 (d, J=8.5Hz, H-2',6'), 7.12 (d, J=8.5Hz, H-3',5'), 3.77 (t, J=7.0Hz, H-7'), 3.49 (d, J=7.0Hz, H-8'), 6.80 (d, J=2.0Hz, H-10', 14'), 6.91 (t, J=2.0Hz, H-12'), 2.31 (1 OAc), 2.28 (2 OAc), 2.27 (1 OAc); ms *m/z* (rel. int.): 622 (13) $M^{+\cdot}$, 580 (15), 538 (8), 496 (2), 454 (2), 433 (5), 392 (10), 349 (3), 312 (10), 279 (10), 264 (4), 227 (15), 213 (7), 206 (7), 189 (27), 149 (38), 147 (42), 121 (20), 111 (20), 71 (100), 42 (50).

Gnetin-B (**3**), yellow crystals, mp 167–172° (purified by tlc). ν max (KBr) cm^{-1}: 3400, 1740, 1580, 1510, 1440, 1370, 1260, 1160, 1000, 960, 830; λ max (MeOH) nm: 256 (ϵ 900), 280 (ϵ 1350), 355 (ϵ 16850).

Gnetin-C (**4a**), yellow crystals, mp 140–141° (purified by tlc) (Found: M 454; $C_{28}H_{22}O_6$ requires: M 454). ν max (KBr) cm^{-1}: 3400, 1610, 1510, 1440, 1360, 1340, 1270, 1230, 1170, 1070, 990, 960, 840; λ max (MeOH) nm: 285 (ϵ 450), 305 (ϵ 450), 320 (ϵ 10900); ^{13}C nmr |22.6 MHz, $(CD_3)_2CO$| δ: 133.0 (s, C-1), 127.9 (d, C-2, 6), 115.5 (d, C-3, 5), 156.9 (s, C-4), 126.0 (d, C-7), 128.4 (d, C-8), 140.4 (s, C-9), 98.7 (d, C-10), 162.1 (s, C-11), 114.3 (s, C-12), 154.3 (s, C-13), 107.3 (d, C-14), 129.2 (s, C-1'), 127.0 (d, C-2', 6'), 115.7 (d, C-3', 5'), 156.9 (s, C-4'), 92.8 (d, C-7'), 55.0 (d, C-8'), 145.3 (s, C-9'), 106.2 (d, C-10', 14'), 158.4 (s, C-11', 13'), 101.4 (d, C-12').

Gnetin-D (**4b**), brown crystals, mp 162–166° (purified by tlc) (Found: M 470; $C_{28}H_{22}O_7$ requires: M 470). ν max (KBr) cm^{-1}: 3400, 1610, 1510, 1450, 1350, 1280, 1150, 1120, 1060, 990, 960, 830, 740; λ max (MeOH) nm: 284 (ϵ 950), 305 (ϵ 250), 320 (ϵ 10700).

Gnetin-E (**7a**), yellow crystals, mp 167–170° (purified by tlc). ν max (KBr) cm^{-1}: 3400, 1600, 1510, 1440, 1360, 1330, 1240, 1170, 1070, 1000, 840; λ max (MeOH) nm: 285 (ϵ 1400), 310 (ϵ 700), 328 (ϵ 23800); ^{13}C nmr (22.6 MHz, $(CD_3)_2CO$) δ: 133.0 (s, C-1), 127.9 (d, C-2, 6), 115.7 (d, C-3,5), 158.2 (s, C-4), 126.0 (d, C-7), 128.4 (d, C-8), 140.4 (s, C-9), 98.6 (d, C-10), 162.0 (s, C-11), 114.3 (s, C-12), 154.4 (s, C-13), 107.2 (d, C-14), 129.6 (s, C-1'), 127.2 (d, C-2', 6'), 115.4 (d, C-3', 5'), 156.9 (s, C-4'), 92.9 (d, C-7'), 55.0 (d, C-8'), 145.1 (s, C-9'), 100.3 (d, C-10'), 161.9 (d, C-11'), 113.5 (s, C-12'), 154.4 (s, C-13'), 107.1 (d, C-14'), 129.2 (s, C-1"), 127.0 (d, C-2", 6"), 115.4 (d, C-3", 5"), 156.9 (s, C-4"), 92.9 (d, C-7"), 55.9 (d, C-8"), 145.6 (s, C-9"), 106.2 (d, C-10", 14"), 158.4 (s, C-11", 13"), 101.4 (d, C-12").

Heptaacetate (**7b**) (**7a**, Ac_2O, C_5H_5N, room temp. 24hr.), slightly yellow crystals, mp 107–110° (purified by tlc). ν max (KBr) cm^{-1}: 1760, 1500, 1440, 1370, 1200, 1010, 900, 800, 750; ^1H nmr (270 MHz, $CDCl_3$) δ: 7.52 (d, J=8.5Hz, H-2,6), 7.10 (d, J=8.5Hz, H-3,5), 7.11 (d,

J=16.5Hz, H-7), 6.97 (d, J=16.5Hz, H-8), 6.81 (bd, J=1Hz, H-10), 7.01 (bd, J=1Hz, H-14), 7.40 (d, J=8.5Hz, H-2',6'), 7.13 (d, J=8.5Hz, H-3',5'), 5.66 (d, J=7.5Hz, H-7'), 4.51 (d, J=7.5Hz, H-8'), 6.48 (d, J=1Hz, H-10'), 6.68 (d, J=1Hz, H-14'), 7.32 (d, J=8.5Hz, H-2", 6"), 7.11 (d, J=8.5Hz, H-3", 5"), 5.53 (d, J=8.5Hz, H-7"), 4.47 (d, J=8.5Hz, H-8"), 6.76 (d, J=2Hz, H-10", 14"), 2.31 (s, 2 OAc), 2.30 (s, 2 OAc), 2.27 (s, 3 OAc).

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