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CHEMICAL CORRELATION OF MORTONINS A, C AND D SESQUITERPENOIDS FROM MORTONIA GENUS†

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Abstract—The structures of mortonins A (**1**), C (**2a**) and D (**3**) were previously deduced from chemical transformations and spectral data. The LAH reductions of mortonin A, mortonin C and their derivatives are discussed. Structure **2a**, previously proposed for mortonin C, is proved by single crystal X-ray diffraction study. The transformation of Mortonin C (**2a**) into Mortonin A (**1**) and Mortonin D (**3**), proves the structure and stereochemistry proposed for all of them.

The Mortonia genus (Celastraceae) is represented by five species in México:[1] *M. gregii* Gray, *M. hidalgensis*, *M. difussa*, *M. palmierii* and *M. scabrella*. We have been studying the sesquiterpene constituents of the aerial part of the first three species mentioned. From all of them we were able to isolate mortonols and mortonins. The mortonols (**4a**, **4b**) have been shown[2,3] to be polyhydroxy derivatives of 6-keto dihydroagarofurane, esterified by acetic and benzoic acids. Mortonins[4,5] (**1a**, **1b**, **2a**, **3**) constitute a new type of sesquiterpene skeleton, which can be related biogenetically to the β-dihydroagarofuane skeleton in which the B ring has suffered an oxidative cleavage to yield a tetrahydrooxepine nucleus as previously postulated.[3,5] The presence of mortonins has been only described in Mortonia species. We think that these type of products could be a chemical guide to include a plant in the Mortonia genus.

The structure of mortonins A (**1a**) and C (**2a**) was fully established previously,[4,5] based on chemical and spectroscopic evidence. The stereochemistry proposed for the different chiral centers of these products, was based on the biogenetic hypotesis[3] and the proton NMR data. The benzoate group attached at C-1, was found to be α-equatorial, as in all the β-dihydroagarofurane derivatives isolated so far from plants which belong to the Celastraceae family. The axial proton at C-1 in both mortonins (**1a** and **2a**) appears as a doublet of doublets at 5.88 with coupling constants (10 and 5 Hz) appropriate for an axial–axial and an axial-equatorial interactions.

The C-4 methyl group was considered to be α-axial and the C-4 hydroxy group β-equatorial, based on the formation of the exocyclic methylene derivative as the sole product obtained on dehydration. This stereochemical assignment agrees with the orientation found for the C-4 substituents in the Celastraceae sesquiterpenoids with a β-dihydroagarofurane skeleton, so far described.[6-8]

The stereochemistry of the C-9 substituents in those compounds has been found to be variable.[6] In mortonin A (**1a**), the C-9 proton appeared at δ 4.65 (J = 7 and 1 Hz) as the X portion of an ABX system which results from the coupling of this proton with the vinylic protons at C-8 and C-7. On catalytic reduction the dihydroderivative **5** obtained, showed H-9 at 4.25 (dd, J = 7 and 1 Hz). The rigidity confered to the oxepane ring by the γ lactone function in Mortonin A, allows for a good measurement of the dihedral angles H-9–H-8, and H-9–H-8′, which are shown to be 25° and 100° when H-9 is ψ-equatorial.

Mortonin C (**2a**) has a benzoate group attached at C-9. In the methyl ester **2b** the H-9 appeared at 6.5 as a doublet of doublets (J = 4 and 1.5 Hz) and was shown[5] to be coupled to the vinylic protons H-8 and H-7. The abnormaly low chemical shift found for H-9 could be explained as a result of the deshielding effect produced by the carbonyl of the ester group at C-5. In the dihydroderivative **6**, H-9 was shifted upfield to 5.25 (dd, J = 10 and 3 Hz). The coupling constants shown by this proton can be explained if the C-9 benzoate is β. The high conformational mobility of the oxepane ring in (**2a**) prevents unambiguous determination of the orientation of 9-benzoate group, whether it is β-ψ equatorial or β-ψ axial, the dihedral angles H-9–H-8 and H-9–H-8′ measured in the Dreiding model could explain the coupling constants found for this proton.

The above discussion indicates that mortonins A (**1a**) and C (**2a**) differ in the stereochemistry at C-9.

In the present report we describe our efforts to correlate both structures.

In the structural elucidation of several β-dihydroagarofurane derivatives isolated from Celastraceae

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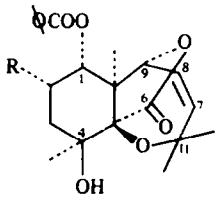
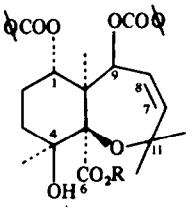
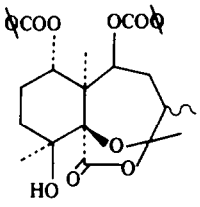


1a: R = H
1b: R = OAc

1



2a: R = H
2b: R = Me



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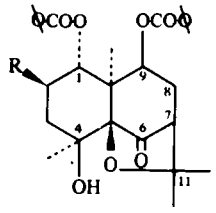
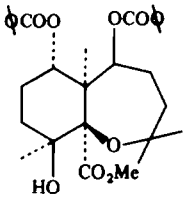


4a: R = H
4b: R = OAc



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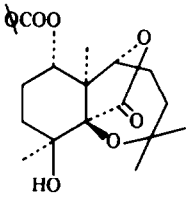

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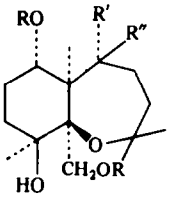
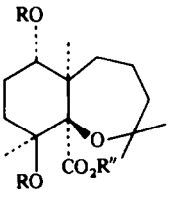


7a: R = H, R′ = OH, R″ = H
7b: R = H, R′ = H, R″ = OH
7c: R = Ac, R′ = OAc, R″ = H
7d: R = Ac, R′ = H, R″ = OAc

7

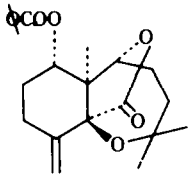
plants, it is a common practice to obtain the related polyols by lithium aluminium hydride treatment of the polyesters.[8] We decided to apply this method to transform dihydromortonins A (**5**) and C (**6**) to the corresponding tetrols, **7a**, 7b.

Treatment of dihydromortonin A, **5**, with a large excess of LAH (1 : 2w) gave a crystalline product which was shown to be the acid diol **8a** on the basis of the following data. On the IR spectrum it showed the characteristic COOH absorption at 2750–3500 and a carbonyl band at 1730 cm^{-1}. In the proton NMR spectrum there were observed three singlets at 1, 1.25 and 1.35 ppm for the four mehtyl groups attached to fully substituted carbon atoms. There was also observed a multiplet (1H) centered at 3.9 ppm which could be ascribed to a proton bound to a carbon atom bearing an hydroxy function. The methyl ester **8b**, showed the methoxy Me at 3.73 (s, 3H). Acetylation of **8b** with Ac_2O and pyridine at room temp (2h) gave the monoacetate derivative **8c**. In its PMR the proton bound to the carbon bearing the acetate group was observed as a doublet of doublets (J = 5 and 10 Hz) at 5.3 ppm. The coupling constants shown by this proton allowed us to deduce that the secondary hydroxy group is at C-1. There was also observed at 3.45 ppm a signal exchangeable with D_2O which was attributed to the C-4 tertiary hydroxy group. Acetylation under more drastic conditions (heating on the steam bath for 4 hr) gave the diacetate derivative **8d**, whose proton NMR spectrum showed the presence of only one proton bound to acetate bearing carbon atom (5.35, dd, J = 5 and



8a: R = R′ = R″ = H
8b: R = R′ = H, R″ = Me
8c: R = Ac, R′ = H, R″ = Me
8d: R = R′ = Ac, R″ = Me

8



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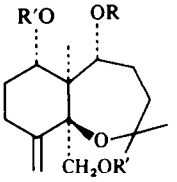
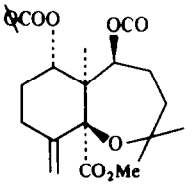


10a: R = R′ = H
10b: R = H, R′ = Ac

10



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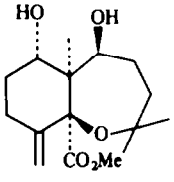

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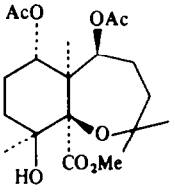

13

10 Hz) and the absence of protons exchangeable with D_2O; the two acetate signals appear at 1.85 and 2 ppm. The isolation of **8a** as the major product obtained by LAH treatment of dihydromortonin A **1**, could be considered as an hydrogenolysis product formed as a result of an intramolecular attack on C-9 of the LAH salt formed by reaction with C-4 hydroxy group.

The expected tetrol **7a** was also produced in a very small yield. The proton NMR spectrum of the triacetate **7c** showed the C-1 proton at 5.29 as a doublet of doublets (J = 10 and 6 Hz) and the C-9 proton as a broad doublet (J = 7 Hz) at 4.94 ppm. The C-6 methylene appeared as an AB q at 4.50 (J = 11 Hz) and 4.90 (J = 11 Hz). The three acetate groups are responsible for two singlets observed at 2.08 (6H) and 2.04 (3H).

In order to examine the influence of the C-4 hydroxy on the LAH reaction, the dihydro anhydromortonin A **9**, was submitted to LAH reaction in the same conditions described above. The triol **10a** was obtained in almost quantitative yield. Acetylation of **10a** gave the diacetate **10b**, which showed in the IR spectrum a strong OH band at 3530 cm^{-1} and carbonyl bands at 1740 ascribed to the acetate groups. In the proton NMR spectrum the exocyclic methylene group is responsible for two broad singlets at 4.54 and 4.92 ppm 1H each. A doublet of doublets centered at 5.45 (J = 5 and 11 Hz) allowed us to localize one of the acetate groups at C-1. The second acetate must be bound to C-6 methylene as the proton NMR showed an AB q (J = 14 Hz) (δ 4.45 and 4.97 ppm); a broad doublet at 3.85 (J = 7 Hz) was attributed to the C-9 proton to which a secondary hydroxy group is attached.

The high yield obtained of the triol **10a** on LAH treatment of dihydro anhydromortonin A **9**, prompted us to submit the methyl ester of dihydro anhydromortonin C **11**, to the same reduction conditions. In the event **11** gave exclusively the ester diol **12**, whose IR spectrum showed a strong OH absorption at 3200 and the ester CO band at 1730 cm^{-1}. In the proton NMR two doublets (J = 2 Hz) at 4.80 and 4.35 were assigned to the exocyclic methylene group; the C-1 and C-9 hydrogens are responsible for two doublets of doublets which appear at 4.55 (J = 6 and 11 Hz) and 4.15 (J = 4 and 10 Hz) respectively. A sharp singlet at 3.70 (3H) can be assigned to the

methyl of the ester group. The resistance of the ester group in **11** to LAH reduction could be due to steric hindrance.

On the other hand treatment of the methyl ester of dihydro mortonin C **6**, with LAH followed by acetylation of the mixture of products obtained, gave rise to two main products. One of them proved to be the diacetate methyl ester **13**. The second product was shown to be the triacetate **7d** of the expected tetrol **7b**. Its proton NMR spectrum showed a multiplet at 5.00 (2H) which can be attributed to the C-1 and C-9 protons, and the typical AB quartet (J = 12 Hz) at 3.80 and 4.51, for the C-6 methylene group. Three singlets at 2.00, 2.05 and 2.10 (3H each) can be ascribed to the three acetate groups present in the molecule.

The absence of hydrogenolysis products in the LAH treatment of mortonin C derivatives, is in agreement with the difference in stereochemistry at C-9 for mortonins A and C deduced from the proton NMR data discussed at the beginning (*vide supra*).

We were able to correlate the structure of mortonin C, **2a** with those of mortonin A **1a** and mortonin D **3**, using acid conditions. Treatments of a solution of mortonin C in benzene with SiO_2 for three days gave mortonin A in 5% yield. Treatment of a benzene solution of mortonin C (**2a**) with boron trifluoride etherate, gave mortonin D (**3**) (10%) and mortonin A (**1a**) in 5% yield, together with other acid catalysed rearrangement products which will be described else where.

Formation of mortonin A (**1a**) on acid treatment of mortonin C (**2a**) can be explained by an intramolecular attack of the carboxyl group at C-9, elimination of the C-9 benzoate group and formation of the γ lactone present in mortonin A (**1a**) with inversion of configuration at this chiral center. Formation of mortonin D (**3**) could be the result of a Wagner Meerwein rearrangement.

The formation of mortonin A (**1a**) on acid treatment of mortonin C (**2a**) proved that both products have the same stereochemistry in all the chiral centers except C-9 as was deduced from the proton NMR data already discussed (*vide supra*).

The structure **3** proposed for mortonin D and the configuration assigned to all the chiral centers except

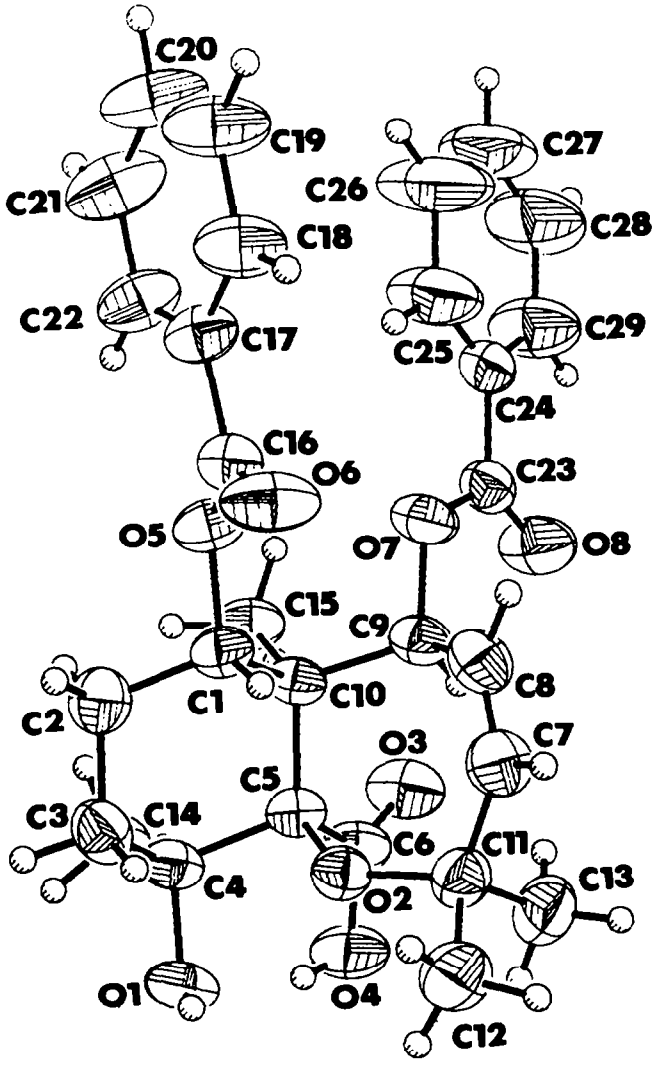

Fig. 1. Molecular structure of Mortonin C. Thermal ellipsoids at 50% probability level.

C-7 and C-11, were based on spectroscopic data. The formation of this product on boron trifluoride treatment of mortonin C (**2a**), confirmed the structure and stereochemistry proposed for it.

An X-ray crystallographic analysis was performed on the Mortonin C to confirm its previously assigned molecular structure on the basis of chemical and spectroscopic evidence.

The geometry of the mortonin C is shown in Fig. 1. The final positional parameters with isotropic temperature factors are listed in Tables deposited with the Cambridge Crystallographic Data Centre.

Single crystals of Mortonin C were crystallized from a methanol solution. Crystal data. $C_{29}H_{32}O_8$, M = 508.22, Orthorombic, a = 11.372(2), b = 13.012(2), c = 18.396(2) Å, V = 2722.2 Å^3 Z = 4, F(OOO) = 1080, $\lambda(CuK_\alpha) = 1.54178$ Å, $\mu(CuK_\alpha) = 7.06$ mm^{-1}, $D_m = 1.315$ Mg m^{-3}, $D_c = 1.239$ Mg m^{-3}, space group $P2_12_12_1$. A crystal was transferred to a Nicolet R3m single- crystal diffractometer with graphite monochromated CuK_α radiation. The orientation matrix and precise cell constants resulted from a least-squares calculation performed using 15 machine-centered reflections. Data collection (θ-2θ scans, background–peak–background, $2\theta < 115°$) yielded 2819 observed independent reflections with $I > 2.5\ \sigma(I)$. A Lorentz and polarization correction but no absorption correction was applied. The structure was solved by direct methods and refined by a cascade-matrix procedure with anisotropic temperature factors for the non-H atoms and with a fixed isotropic temperature factor, $U = 0.06$ Å^2, for the H atoms, to converge with a weighted R = 0.045 (unweighted R = 0.056). The function minimized was $\Sigma w[\Delta F]^2$ with a weighting scheme $w^{-1} = |\sigma^2(F_0) - K(F_0)^2|$ with a final K value of 0.001235. Calculations were carried out on a Nova 4 computer and plots were drawn on a Tektronix plotter. The program package was SHELXTL.[10] Detailed results will be published elsewhere.

EXPERIMENTAL

M.ps are uncorrected IR spectra were recorded in $CHCl_3$ ^{1}H NMR spectra were recorded in $CDCl_3$ using TMS as int. standard, chemical shifts are given in δ. Analysis were determined by Dr. F. Pascher, Bonn, Germany.

Isolation of Mortonin A, **1**. Mortonin A, **1**, was isolated from *Mortonia gregii* (Gray) as previously described.[9]

LAH treatment of dihydromortonin A, **5**. Product **5** was obtained by catalytic hydrogenation of Mortonin A, **1**, as previously described.[4] A solution of **5** (500 mg) in THF (25 ml) was added with stirring to a suspension of LAH (500 mg) in THF (50 ml) under ice bath cooling. The mixture was stirred at room temp for 2 h and diluted with AcOEt and a few drops of sat Na_2So_4 aq soln. The ppts formed were filtered off and washed with AcOEt. Evaporation of the organic solvents gave a semicrystalline residue (IR showed COOH absorption in the 2700–3500 region and 1725 cm^{-1}) which was treated with ethereal diazomethane and separated by a tlc (silica gel) with acetone–$CHCl_3$ (1:9). Crystallization from acetone, n-hexane gave **8b** (100 mg), m.p. 129–130°; ν_{max} 3550 (OH), 1730 (CO); ^{1}H NMR: 3.90 (m, 1H) H-1, 3.75 (s, 3H) ester Me, 3.40 (br, s, 1H) which disappear with D_2O is due to C_4-OH; 1.25, 1.28, 1.35 and 1.45 (4s, 3H each) C-11 gem-dimethyl and Me at C-4 and C-10. (Found: C, 63.38; H, 9.37; O, 26.70; Calc for $C_{16}H_{28}O_5$: C, 63.97; H, 9.40; O, 26.63%.)

Treatment of **8b** (20 mg) with Ac_2O (0.5 ml) and pyridine (0.5 ml) for 4 h at room temp, followed by normal work up gave **8c**, ν_{max} 3550 (OH), 1745 cm^{-1} (CO's); ^{1}H NMR: 5.35 (dd, J = 5 and 10 Hz, 1H) H-1; 3.72 (s, 3H) ester Me; 3.48 (1H) disappear with D_2O is due to C_4-OH; 2.00 (s, 3H) acetyl Me; 1.41 and 1.30 (2s, 6H each) due to C-11 gem-dimethyl and C-4 and C-10 Me groups. MS, *m/z*: 283.3 (M$^+$-59, 2.7), 282 (12) 224 (10); 193 (10); 177 (11), 155 (20); 135 (25); 95 (54.5); 82.2 (61.4); 43.1 (100); $C_{18}H_{30}O_6$ requires (M$^+$) at 342.

Treatment of **8b** (20 mg) with Ac_2O (0.5 ml) and pyridine (0.5 ml) on the steam bath for 4 h, gave **8d**, m.p. 102–104°; ν_{max} 1725 cm^{-1} (CO's); ^{1}H NMR; 5.35 (dd, J = 5 and 10 Hz, 1H); 3.70 (s, 3H) ester Me; 2.00 (s, 3H) C-1 acetyl Me; 1.90 (s, 3H) C-4 acetyl Me; 1.70, 1.40, 1.35, 1.25 (4s, 3H each) C-11 gem-dimethyl, C-4 and C-10 Me groups. MS *m/z*: 384.5 (M$^+$, 1.2); 369.5 (8.1), 342 (40), 325 (40), 325 (M$^+$-59, 18); 282.4 (325-43, 100%); 265 (22); 205 (50), 193 (30), 177 (40) 135 (52); $C_{20}H_{32}O_7$ requires (M$^+$) at *m/z* 384.5.

In one experiment the mixture of LAH reduction of **5** (500 mg) was acetylated (Ac_2O, pyridine, room temp, overnight) and the product obtained was separated by column chromatography and preparative tlc (silica gel). The triacetate **7c** (25 mg) was obtained and crystallized from acetone-hexane; m.p. 170–175°; ν_{max} 3500 (OH), 1745 (CO's); ^{1}H NMR; 5.29 (dd, J = 6, 10 Hz, 1H) H-1, 4.94 (brd J = 7 Hz, 1H, H-9), 4.90 (1H, J = 11 Hz) and 4.50 (1H, J = 11 Hz) C-6 methylene AB q; 2.06 and 2.04 (2s, 9H) 3 acetyl Me's; 1.40, 1.35 and 1.25 (3s, 12H) C-11 gem-dimethyl group and C-4 and C-10 Me groups. MS, *m/z*: 339.4 (M$^+$-CH_2OAc-H; 0.8), 312.4 (1.3) 299.3 (1.0); 295.4 (2.6); 281 (1); 221 (5); 183.3 (45.4); 138.3 (100), $C_{21}H_{34}O_8$ requires (M$^+$) at *m/z* 414.

LAH treatment of anhydro dihydro mortonin A, **9**. Product **9** was obtained as previously described.[4]

A solution of **9** (100 mg) in THF (10 ml) was added with stirring to a suspension of LAH (200 mg) in THF (15 ml) under ice bath cooling. The reaction mixture was stirred at room temp for 4 h and treated as for **5** (*vide supra*). Elimination of the organic solvents gave an oily residue which was separated by preparative TLC (silica gel) with AcOEt. Product **10a** (70 mg) was recrystallized from $CHCl_3$–acetone; m.p. 185–188°; ν_{max} 3250 (br. band, OH's). (Found: C, 66.03; H, 9.69; Calc for $C_{15}H_{26}O_4$: C, 65.88; H, 9.44%.)

Acetylation of **10a** (Ac_2O, py, room temp overnight) gave **10b** after the usual work up. The pure sample was obtained from aceton–hexane, m.p. 170–174°; ν_{max} 3550 (OH), 1740 (br band, CO's) 1660 and 910 cm^{-1} (exocyclic methylene double bond), ^{1}H NMR: 5.45 (dd, J = 5 and 11 Hz, 1H); 4.92 and 4.54 (2 br, s, 1H each) C-14 vinylic protons; 4.97 and 4.55 (ABq, J-14 Hz, 2H) C-6 methylene, 3.85 (m, 1H) H-9; 2.05 and 2.00 (2s, 3H each) acetyl Me's; 1.36, 1.25 and 1.10 (3s, 3H each) C-11 gem-dimethyl and Me at C-10. MS, *m/z*: 294.4 (M$^+$-60; 4.3); 281.3 (M$^+$-73; 0.8); 225.3 (100), 191 (23); 165 (75); 99.2 (94.7); $C_{19}H_{30}O_6$ requires (M$^+$) at *m/z* 354.

Isolation of mortonin C, **2a**. Mortonin C, **2a**, was isolated from *M. hidalgensis* as previously described.[3]

Preparation of the methyl ester of mortonin C, **2b**. Treatment of **2a** with ethereal diazomethane gave the methyl ester **2b** in quantitative yield. Crystallized from AcOEt–hexane it showed m.p. 120–121°, ν_{max} 3550 (OH), 1725 (CO,s), 1605 and 1590 (aromatic double bonds); ^{1}H NMR: 7.1–8.1 (m, 10H) aromatic protons, 6.45 (dd, J = 2 and 4 Hz, 1H) H-9; 5.84 (dd, J = 5 and 12 Hz, 1H) H-1; 5.75 (dd, J = 2 and 12 Hz, 1H) H-7; 5.40 (dd, J = 4 and 12 Hz, 1H) H-8; 3.76 (s, 3H) ester Me; 1.72, 1.54, 1.44 and 1.35 (4s, 12H) C-11 gem-dimethyl and Me's at C-4 and C-10. (Found: C, 68.50; H, 6.54; O, 24.75; Calc for $C_{30}H_{34}O_8$: C, 68.95; H, 6.56; O, 24.49%.)

Catalytic hydrogenation of **2b**. The methyl ester **2b** (500 mg) in AcOEt was catalytically hydrogenated using 10% Pd/C (50 mg) as catalyst. The catalyst was filtered off and the solvent removed under vacuum. The crystalline

product **6** (475 mg) showed m.p. 166–167°; ν_{max} 3540 (OH), 1745 and 1710 (CO's), 1605 and 1580 (aromatic double bonds); ^{1}H NMR 6.70–8.20 (m, 10H) aromatic protons; 6.1 (m, 1H) H-1; 5.25 (dd, J = 2.5 and 11 Hz) H-9; 3.86 (s, 3H) Me ester; 3.51 (br d, 1H) which disappeared with D_2O is due to C_4-OH; 1.62 and 1.50 (2s, 12H) 4 Me groups. MS *m/z* 524 (M^+). 446 (M^+-78), 402 (M^+-122), 280 (402-122), 220, 149 and 105 (100%), $C_{30}H_{36}O_8$ requires (M^+) at *m/z* 524.

Anhydro dihydromortonin C methyl ester, **11**. A soln of **6** (500 mg) in pyridine (10 ml) was treated with $SOCl_2$ (1 ml) in an ice bath for 1 h, poured onto ice and extracted with AcOEt. The organic soln was washed with dil HCl, sat $NaHCO_3$ aq soln and water, dried and the solvent removed under vacuum. The solid product obtained was recrystallized from AcOEt–hexane to yield **11** (400 mg), m.p. 184–185° ν_{max} 1735 and 1710 (CO's), 1650, 910 (exocyclic methylene), 1605, 1585 (aromatic double bonds); ^{1}H NMR: 6.80–8.15 (aromatic protons); 6.22 (dd, J = 5 and 10 Hz, 1H) H-1; 5.70 (dd, J = 2 and 12 Hz) H-9; 5.00 (d, J = 2 Hz, 1H) and 4.50 (d, J = 2 Hz, 1H) C-14 vinylic protons; 3.84 (s, 3H) ester Me; 1.62 and 1.46 (2s, 9H) C-11 gem-dimethyl and Me at C-10. MS: *m/z* 506.7 (M^+), 447 (M^+-59), 384 (M^+-122), 262 (384–122), 325 (447–122) 105 (100%), $C_{28}H_{34}O_7$ requires (M^+) at *m/z* 506.7.

LAH treatment of **11**. A soln of **11** (100 mg) in THF (10 ml) was treated with LAH as described for **5** (*vide supra*). The solid product obtained in quantitative yield, was recrystallized from $CHCl_3$–hexane to yield **12**, m.p. 188–189°; ν_{max} 3200 (br s, OH's), 1730 (CO of the C-5 carbomethoxy), 1650 and 905 (C-4 exocyclic methylene); ^{1}H NMR: 4.90 (d, J = 2 Hz, 1H) and 4.35 (d, J = 2 Hz, 1H) C-4 exocyclic methylene; 4.55 (dd, J = 5 and 10 Hz, 1H) H-1; 4.15 (dd, J = 4 and 10 Hz, 1H) H-9 3.70 (s, 3H) ester Me; 3.20 (2H) disappeared on D_2O addition is due to C-1 and C-9 OH's; 1.35 (s, 9H) C-11 gem-dimethyl and Me at C-10. MS, *m/z*: 280 (M^+-18), 283 (M^+-15), 265 (283–18), 181 (265–84), 150 (181–31) (100%). (Found: C, 64.10; H, 8.62: O, 26.7; Calc for $C_{16}H_{26}O_5$: C, 64.40; H, 8.78; O, 26.81%.)

LAH treatment of **6**. The dihydromortonin C mehtyl ester **6** (500 mg) in THF (25 ml) was treated with LAH as described for **5**. The semisolid product obtained was washed with hexane acetylated in normal conditions (Ac_2O, pyridine room temp 1 h) to yield a mixture of products which were separated by preparative tlc (silica gel) using AcOEt–hexane (6 : 4) as eluent.

Product **13** was obtained in 55% yield; m.p. 148–150°; ν_{max} 3450 (OH), 1730 (acetate CO's), 1705 (methyl ester CO); ^{1}H NMR; 5.65 (dd, J = 6 and 10 Hz, 1H) H-1; 4.65 (dd, J = 4 and 6 Hz, 1H) H-9; 3.85 (s, 3H) ester Me; 3.65 (br. s, 1H) exchangeable with D_2O due to C_4-OH; 2.05 and 1.95 (2s, 3H each) acetyl Me's at C-1 and C-9; 1.40 and 1.15 (2s, 9 and 3H) C-11 gem-dimethyl and Me's at C-4 and C-10. MS *m/z*: 340 (M^+-60, 12.2), 280 (340–60, 2), 262 (280–181), 199, (25), 179 (36), 135 (22), 43 (100) $C_{20}H_{32}O_8$ requires (M^+) at *m/z* 400.

The triacetate **7d** was isolated in 17% yield as an oily product ν_{max} 3500 (OH), 1730 (CO's); ^{1}H NMR: 5.00 (m, 2H) H-1 and H-9; 4.55 and 4.78 (q, J = 12 Hz, 2H) C-6 methylene; 2.12, 2.08 and 2.00 (3s, 3H each) acetyl Me's; 1.25, 1.20, 1.17 and 1.08 (4s, 3H each) C-11 gem-dimethyl and Me's at C-4 and C-10. MS, *m/z*: 338 (M^+-76, 2.5), 278 (338–60, 0.4), 218 (218–60, 15), 177 (34), 162 (48), 149 (41.6), $C_{21}H_{34}O_8$ requires (M^+) at *m/z* 414.

Treatment of mortonin C with SiO_2. A soln of **2a** (100 mg) in benzene was treated with SiO_2 (1 g) at room temp for 3 days, filtered and the solvent removed under vacuum. The recovered **2a** was separated by crystallization. The mother liquors showed the presence of Mortonin A, **1**, which was purified by TLC (silica gel) (yield 5%) and identified by comparison with an authentic sample.

Treatment of mortonin C with $BF_3 \cdot Et_2O$. $BF_3 \cdot Et_2O$ (0.4 ml) was added to a cold (ice bath) solution of **2a** (100 mg) in benzene (10 ml). The reaction was stirred at room temp for 24 hr, poured onto ice and extracted with AcOEt. The organic layer was extracted with sat $NaHCO_3$ aq soln, washed with water, dried and the solvent removed. The neutral fraction was separated by TLC (silica gel). Mortonin A, **1** (5 mg) and Mortonin D, **3** (10 mg) were obtained and identified by comparison with authentic samples.

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