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THE STRUCTURE OF CORYLIFURAN, A CLERODANE-TYPE DITERPENE FROM *CROTON CORYLIFOLIUS* LAM

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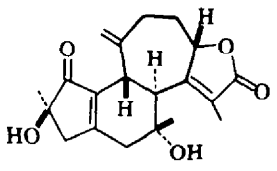
Abstract—The structure and stereochemistry of corylifuran, a clerodane-type diterpene from *Croton corylifolius* Lam, have been determined as **2** by chemical and spectroscopic data and X-ray crystallographic analysis.

Our recent examination of the leaves and twigs of *Croton corylifolius* Lam (Euphorbiaceae) has led to the isolation of the diterpene crotofolin A **1** which was shown to possess a new carbon skeleton (crotofolane).[1] Further scrutiny of this plant has led to the isolation of another diterpene, corylifuran **2**, whose structure and stereochemistry are now reported. It will be shown that corylifuran belongs to the clerodane group of diterpenoids, a group in which there is now much current interest.[2]



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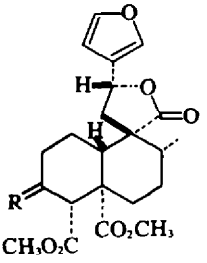
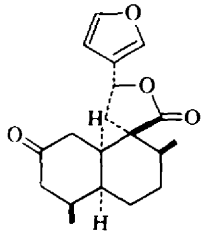


2: R = O
7: R = H, α-OH

Corylifuran **2**, m.p. 181–184°, $[\alpha]_D + 44°$, has the molecular formula $C_{22}H_{26}O_8$ from combustion analysis and high resolution mass spectrometry. The spectral properties indicated the presence of a secondary Me group (3 H, doublet, J = 7 Hz at δ 1.01), two CO_2Me groups (ν_{max} 1739 cm^{-1}, singlets of 3 H each at 3.73 and 3.78), a γ-lactone (ν_{max} 1758 cm^{-1}) and a β-substituted furan [λ_{max} 210 nm (ε 6600), ν_{max} 1503, 875 cm^{-1}, narrow multiplets at 7.47 (2 H) and 6.48 (1 H)]. In addition, there was a singlet at δ 3.23 (which will be referred to later) and a triplet at 5.38 (J = 8 Hz) which suggested that the relationship of the furan and the lactone moieties was as found in crotonin **3**.[3] This was supported by the mass spectral fragmentation pattern. The base peak at *m/e* 94 and other significant peaks at *m/e* 81 (60%) and 95 (64%) may be attributed to the fragments **4**, **5** and **6** respectively; precise mass measurements were in accord.



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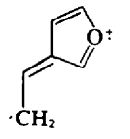

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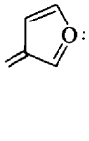

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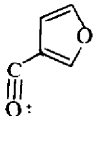

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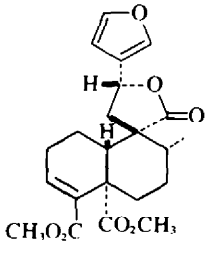
The natural abundance Fourier transform ^{13}C NMR spectrum (Table 1) was in agreement with the above functionalities. It had resonances for the β-substituted



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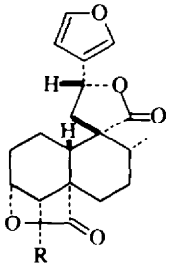

9: R = CH_2OH
10: R = CH_2OAc
11: R = CO_2H
12: R = CO_2Me

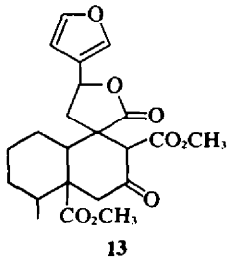

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Table 1. ^{13}C chemical shifts of corylifuran (2, $CDCl_3$)[a]

C - 1	39.4 (t)[b]	C - 12	71.9 (d)
C - 2	41.9 (t)	C - 13	124.9 (s)
C - 3	201.7 (s)	C - 14	107.9 (d)
C - 4	68.2 (d)	C - 15	143.9 (d)
C - 5	51.8 (s)	C - 16	139.4 (d)
C - 6	23.8 (t)[b]	C - 17	17.0 (q)
C - 7	33.4 (t)[b]	C - 18	171.0 (s)[c]
C - 8	39.4 (d)	C - 19	167.7 (s)[c]
C - 9	50.4 (s)	C - 20	175.9 (s)
C -10	50.7 (d)	C - 21	51.1 (q)[c]
C -11	27.2 (t)	C - 22	51.8 (q)[c]

a. - Chemical shifts are in p.p.m. from T.M.S.

b. - Assignments tentative.

c. - Assignments may be reversed.

furan, one C-methyl, two carbomethoxy groups together with the lactone and ketone carbonyl groups. In addition there were two singlets for quaternary carbons, four methine doublets and five methylene triplets. The assignments are based on the chemical shifts and the multiplicities observed in the offset decoupled spectra.

As there was no evidence of further unsaturation in the molecule, corylifuran must be bicarbocyclic. This, taken together with the identification of the furan-γ-lactone system and other structural features in the spectral data presented, could be rationalised if corylifuran were a clerodane-type diterpene. The bicarbocyclic system must then accommodate a ketone and the gross structure would be complete if two of the carbons attached at C-4, 5 and 8 were further modified as carbomethoxy groups and the other was a Me group. The relationship between these groups were established in the following way.

Corylifuran can be recovered from treatment with 2N H_2SO_4 or 5% KOH in methanol at reflux for 1 hr (followed by acidification); more vigorous treatment with base led to a complex mixture from which no useful result could be obtained. It gave no colour with ferric chloride under the usual conditions, but the addition of dilute alkali led to the progressive development of a new max at 283 nm (ε 9000) due to the enolate ion; the apparent pK_a being 12.84. This result is in agreement with the β-keto ester moiety of **2** and the one proton singlet at 3.23 in the NMR spectrum of corylifuran can now be ascribed to H-4.

Reduction of corylifuran with sodium borohydride gave, as the major product, the corresponding alcohol **7**, m.p. 195–198°. The configuration (axial) of this alcohol follows from the appearance of the carbinol proton as a narrow multiplet ($W_{1/2}$ = 8 Hz) at δ 4.22. Mild treatment of the alcohol with thionyl chloride afforded the α,β-unsaturated ester **8**, $C_{22}H_{26}O_7$, m.p. 200–202°, with the expected spectral properties.

The location of the second carbomethoxy group and its relative configuration were demonstrated as follows. Further treatment of the alcohol **7** with sodium borohydride afforded the dilactone alcohol **9**, $C_{20}H_{24}O_6$, m.p. 199–202°, ν_{max} 3363, 1770, 1755 cm^{-1}. Given the configuration of the starting alcohol, the genesis of the new γ-lactone required that the second carbomethoxy group be also axial. The NMR spectrum of the derived acetate **10** clearly showed the AB part of an ABX system (δ 4.10, 4.30; J_{AB} 13.0, J_{AX} 9.0, J_{BX} 5.0 Hz). Jones oxidation of the dilactone alcohol **9** gave the acid **11** which was further characterised as its methyl ester **12**.

The evidence which has been presented is also compatible with structure **13** for corylifuran. A decision between the alternatives was made, and the relative configuration established, by an X-ray crystallographic analysis of corylifuran.

Corylifuran **2** crystallised from methanol in the unambiguously determined space group $P2_1$ with a = 11.641(4), b = 11.834(4), c = 7.642(4) Å and β = 104.45(2)°. A calculated and measured density indicated one molecule per asymmetric unit. A total of 1459 unique reflections with $\theta \leq 114°$ were measured using an ω-scan technique and graphite monochromated CuK_α (1.5418 Å) X-rays. A total of 1434 reflections were judged observed [$F_0 \geq 3\sigma(F_0)$] after correction for background, Lorentz and polarisation effect.

The structure was solved with some difficulty using a weighted tangent formula approach and recycling of plausible molecular fragments.[4] Full-matrix, least-squares refinements with anisotropic temperature factors, for nonhydrogen atoms and isotropic temperature factors for hydrogens smoothly converged to the current X-ray model which has a standard crystallographic residual of 4.9% for the observed reflections.[5]

A computer generated drawing of the X-ray model is presented in Fig. 1 and final fractional coordinates, bond lengths and bond angles are given in Tables 2–4 respectively.

The CD spectrum of corylifuran in ethanol shows a positive Cotton effect (Δε + 2.26 at 282 nm) and the absolute configuration, as written into **2**, follows from the application of the octant rule.[6]

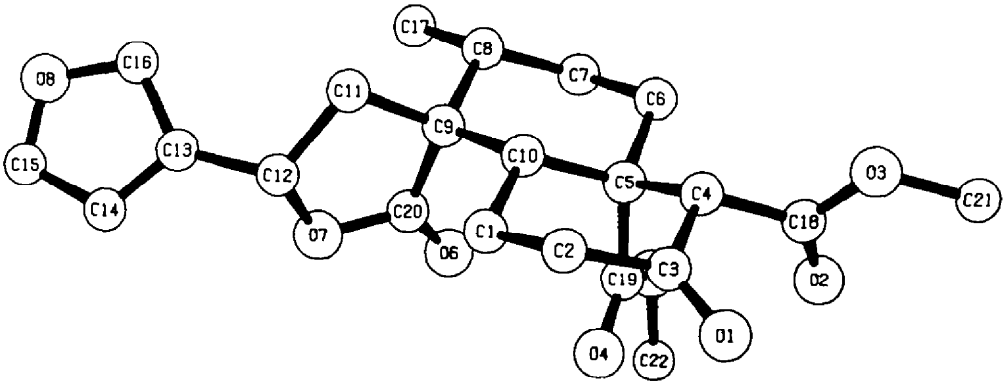

Fig. 1.

Table 2. Final fractional coordinates for corylifuran. The estimated standard deviation is given in parenthesis and hydrogen atoms are numbered the same as the atom to which they are attached

Atom	X	Y	Z
C(1)	0.3801(3)	0.2012	0.5494(4)
C(2)	0.5151(3)	0.1828(6)	0.6265(5)
C(3)	0.5765(3)	0.1529(5)	0.4816(4)
C(4)	0.5464(2)	0.2291(4)	0.3152(4)
C(5)	0.4103(2)	0.2409(4)	0.2312(3)
C(6)	0.3884(2)	0.3326(4)	0.0851(3)
C(7)	0.2575(3)	0.3627(4)	0.0169(4)
C(8)	0.2016(2)	0.4014(4)	0.1658(4)
C(9)	0.2211(2)	0.3157(4)	0.3241(3)
C(10)	0.3549(2)	0.2810(4)	0.3870(3)
C(11)	0.1780(3)	0.3645(5)	0.4862(4)
C(12)	0.1067(3)	0.2708(4)	0.5451(4)
C(13)	-0.0055(3)	0.3051(5)	0.5891(4)
C(14)	-0.0764(8)	0.2388(6)	0.6540(1)
C(15)	-0.1740(5)	0.2958(6)	0.6770(1)
C(16)	-0.0630(4)	0.4093(5)	0.5758(8)
C(17)	-0.0703(3)	0.4299(5)	0.0862(5)
C(18)	0.6159(2)	0.1890(4)	0.1839(4)
C(19)	0.3686(2)	0.1229(4)	0.1593(4)
C(20)	0.1408(2)	0.2129(4)	0.2725(4)
C(21)	0.7968(4)	0.2056(6)	0.1016(8)
C(22)	0.2904(5)	0.0081(5)	-0.0896(6)
O(1)	0.6488(2)	0.0785(4)	0.4962(4)
O(2)	0.5821(2)	0.1145(4)	0.0757(4)
O(3)	0.7167(2)	0.2449(4)	0.2066(3)
O(4)	0.3793(2)	0.0413(4)	0.2588(3)
O(5)	0.3258(2)	0.1187(4)	-0.0180(3)
O(6)	0.1270(2)	0.1555(4)	0.1396(3)
O(7)	0.0780(2)	0.1921(4)	0.3941(3)
O(8)	-0.1635(4)	0.3955(7)	0.6325(6)
H(1A)	0.333(4)	0.120 (4)	0.503 (5)
H(1B)	0.353 (4)	0.235 (5)	0.648 (7)
H(2A)	0.534 (4)	0.133 (4)	0.712 (6)
H(2B)	0.543 (5)	0.262 (6)	0.689 (8)
H(4)	0.573 (3)	0.288 (4)	0.349 (4)
H(6A)	0.428 (3)	0.402 (4)	.128 (4)
H(6B)	0.413 (3)	0.316 (3)	-0.037 (4)
H(7A)	0.219 (3)	0.303 (3)	-0.055 (5)
H(7B)	0.241 (4)	0.413 (4)	-0.077 (6)
H(8)	0.249 (4)	0.468 (4)	0.222(6)
H(10)	0.397(4)	0.355(4)	0.418(5)
H(11A)	0.134(3)	0.435(3)	0.457(5)
H(11B)	0.250(5)	0.389(5)	0.567(7)
H(12)	0.146(3)	0.237(4)	0.650(5)
H(14)	-0.036(9)	0.180(1)	0.720(1)
H(15)	-0.210(2)	0.150(2)	0.710(3)
H(16)	-0.049(6)	0.457(7)	0.510(9)
H(17A)	0.055(6)	0.492(6)	-0.019(8)
H(17B)	0.025(5)	0.468(6)	0.148(8)
H(17C)	0.041(4)	0.366(5)	0.037(6)
H(21A)	0.826(7)	0.116(8)	0.130(1)
H(21B)	0.767(9)	0.216(9)	-0.010(1)
H(21C)	0.070(1)	0.220(2)	0.150(2)
H(22A)	0.362(8)	-0.049(9)	-0.040(1)
H(22B)	0.248(8)	0.005(9)	-0.270(1)
H(22C)	0.226(5)	-0.010(5)	-0.043(7)

Table 3. Bond lengths in corylifuran. The estimated standard deviation is given in parentheses

C(1) - C(2)	1.549(5)	C(18) - O(2)	1.201(4)
C(1) - C(10)	1.529(4)	C(18) - O(3)	1.320(4)
C(2) - C(3)	1.501(5)	O(3) - C(21)	1.451(5)
C(3) - C(4)	1.527(5)	C(19) - O(4)	1.216(4)
C(3) - O(1)	1.205(5)	C(19) - O(5)	1.323(4)
C(4) - C(5)	1.559(4)	O(5) - C(22)	1.439(5)
C(4) - C(18)	1.514(4)	C(11) - C(12)	1.519(5)
C(5) - C(6)	1.533(4)	C(12) - O(7)	1.456(4)
C(5) - C(10)	1.562(4)	C(12) - C(13)	1.489(5)
C(5) - C(19)	1.534(4)	O(7) - C(20)	1.340(4)
C(6) - C(7)	1.524(4)	C(20) - O(6)	1.198(4)
C(7) - C(8)	1.516(4)	C(13) - C(14)	1.320(7)
C(8) - C(9)	1.551(4)	C(13) - C(16)	1.393(6)
C(8) - C(17)	1.536(5)	C(14) - C(15)	1.369(8)
C(9) - C(10)	1.566(4)	C(15) - O(8)	1.242(9)
C(9) - C(11)	1.559(4)	O(8) - C(16)	1.354(8)
C(9) - C(20)	1.525(4)		

Table 4. Bond angles in corylifuran. The estimated standard deviation is given in parentheses

C(2) - C(1) - C(10)	111.5(3)
C(1) - C(2) - C(3)	112.1(3)
C(2) - C(3) - C(4)	115.0(3)
C(2) - C(3) - O(18)	123.6(3)
C(4) - C(3) - O(1)	121.1(3)
C(3) - C(4) - C(5)	113.2(2)
C(3) - C(4) - C(18)	108.5(3)
C(5) - C(4) - C(18)	114.3(2)
C(4) - C(5) - C(6)	109.3(2)
C(4) - C(5) - C(10)	106.5(2)
C(4) - C(5) - C(19)	105.3(2)
C(6) - C(5) - C(10)	108.3(2)
C(6) - C(5) - C(19)	113.8(2)
C(10) - C(5) - C(19)	113.3(2)
C(5) - C(6) - C(7)	112.6(2)
C(6) - C(7) - C(8)	113.2(2)
C(7) - C(8) - C(9)	112.4(2)
C(7) - C(8) - C(17)	109.9(2)
C(9) - C(8) - C(17)	112.9(3)
C(8) - C(9) - C(10)	110.5(2)
C(8) - C(9) - C(11)	111.3(2)
C(8) - C(9) - C(20)	111.1(2)
C(10) - C(9) - C(11)	110.2(2)
C(10) - C(9) - C(20)	111.7(2)
C(11) - C(9) - C(20)	101.7(2)
C(1) - C(10) - C(5)	113.4(2)
C(1) - C(10) - C(9)	112.7(2)
C(5) - C(10) - C(9)	114.4(2)
C(4) - C(18) - O(2)	124.7(3)
C(4) - C(18) - O(3)	111.1(3)
O(2) - C(18) - O(3)	124.2(3)
C(18) - O(3) - C(21)	116.0(3)
C(5) - C(19) - O(4)	121.6(2)
C(5) - C(19) - O(5)	114.0(2)
O(4) - C(19) - O(5)	124.3(3)
C(19) - O(5) - C(22)	115.0(3)
C(9) - C(11) - (12)	105.8(3)
C(11) - C(12) - O(7)	105.4(2)
C(11) - C(12) - C(13)	116.4(3)
O(7) - C(12) - C(13)	108.2(3)
C(12) - O(7) - C(20)	112.1(2)
C(9) - C(20) - O(7)	111.8(2)
C(9) - C(20) - O(6)	127.9(3)
O(7) - C(20) - O(6)	120.2(3)
C(12) - C(13) - C(14)	126.1(4)
C(12) - C(13) - C(16)	131.0(4)
C(14) - C(13) - C(16)	102.9(4)
C(13) - C(14) - C(15)	111.7(6)
C(14) - C(15) - O(8)	107.0(5)
C(15) - O(8) - C(16)	110.8(4)
C(13) - C(16) - O (8)	107.7(5)

EXPERIMENTAL

M.ps were determined on a Kofler hot-stage apparatus and are uncorrected. UV and IR spectra were determined in EtOH and $CHCl_3$ respectively. NMR spectra were done in $CDCl_3$, unless otherwise stated, with TMS as internal reference. The ^{13}C NMR spectrum was recorded on a Varian XL-100 instrument operating at 25.2 M Hz.

All evaporations were carried out at reduced pressure.

Isolation of corylifuran **2**. Dried, finely ground leaves and twigs of *Croton corylifolius* (voucher specimen No. IJ 47787, Institute of Jamaica) (3.5 kg) was extracted by percolation with benzene (20 *l*). The residue (150 g) which was obtained by evaporation of the solvent, was chromatographed on Al_2O_3 (III, 2.2 kg) with benzene–EtAc (4:1) as eluent to give a mixture (17 g). Rechromatography on Al_2O_3 with benzene and benzene–EtAc (4:1) afforded a product (2.30 g) from which *corylifuran* **2** crystallised as prisms from light petroleum–acetone, m.p. 181–184°; $[\alpha]_D + 44°$ $CHCl_3$, c = 0.9); ν_{max} 1758 (γ-lactone), 1739 (ester), 1715 (cyclohexanone), 1503, 875 (furan) cm^{-1}; δ 1.02 (3 H, d, J = 7.0 Hz, *sec*-Me), 3.23 (1 H, s, H-4), 3.73 and 3.78 (3 H each, s, $2CO_2Me$), 5.38 (1 H, t, J = 8 Hz, H-12), 6.43 (1 H, m, H-14), 7.47 (2 H, m, H-15 and H-16). [Found: C, 62.9; H, 6.3; M^+, *m/e* 418.1654. $C_{22}H_{26}O_8$ requires: C, 63.15; H, 6.3%; *M*, 418.1620].

The alcohol **7**. A soln of corylifuran (52 mg) and $NaBH_4$ (50 mg) in 95% EtOH (5 ml) was kept at room temp. for 1 hr. The product, isolated in the usual manner and shown to be predominantly one compound by TLC, recrystallised from light petroleum–acetone as cubes, m.p. 195–198°; λ_{max} 210 nm (ϵ = 6200); ν_{max} 3320, 1757, 1730, 1500 and 877 cm^{-1}; δ 0.99 (3 H, d, J = 7 Hz, *sec*-Me), 3.75 and 3.90 (3 H each, $2CO_2Me$), 4.22 (1 H, m, $W_{1/2}$ = 8 Hz, H-3), 5.20 (OH), 5.42 (1 H, t, J = 8 Hz, H-12), 6.43 and 7.48 (1 H and 2 H respectively, m, furan). (Found: C, 63.5; H, 6.6; $C_{22}H_{28}O_8$ requires: C, 62.8; H, 6.7%).

The olefin **8**. Thionyl chloride (5 drops was added to a soln of 7

(230 mg) in pyridine (5 ml) and the mixture kept at room temp. for 20 min. After dilution with 3N HCl, the product was extracted with $CHCl_3$ and purified by preparative-scale TLC. The olefin (70 mg) crystallised from light petroleum–acetone as prisms, m.p. 200–202°; λ_{max} 209 nm (ϵ = 10,500); ν_{max} 1765, 1725, 1500 and 879 cm^{-1}; δ 1.00 (3 H, d, J = 7 Hz, *sec*-Me), 3.68 and 3.73 (3 H each, $2CO_2Me$) 5.35 (1 H, t, J = 8 Hz, H-12), 6.76 (1 H, m, $W_{1/2}$ = 8 Hz, H-3), 6.37 and 7.38 (1 H and 2 H respectively, furan). (Found: C, 65.8; H, 6.3; M^+, *m/e* 402. $C_{22}H_{26}O_7$ requires C, 65.7; H, 6.5%; *M*, 402).

The dilactone alcohol **9**. A soln of corylifuran (46 mg) and $NaBH_4$ (45 mg) in EtOH (10 ml) was kept at room temp. for 3 days. The product (34 mg), isolated in the usual way, crystallised from light petroleum–acetone to give the *dilactone alcohol* **9** as prisms, m.p. 199–202°; λ_{max} 210 (ϵ = 5600); ν_{max} 3363, 1770, 1755, 1505 and 883 cm^{-1}; δ (C_5D_5N) 1.05 (3 H, d, J = 7 Hz, *sec*-Me), 3.87 (2 H, m, H-18), 5.00 (1 H, m, $W_{1/2}$ = 6 Hz, H-3), 5.50 (1 H, t, J = 9 Hz, H-12), 5.97 (OH), 6.60 and 7.60 (1 H and 2 H respectively, furan). (Found: C, 66.9; H, 6.4. $C_{20}H_{24}O_6$ requires: C, 66.65; H, 6.7%).

The dilactone alcohol **9** could also be obtained by reduction of the alcohol **7** under similar conditions.

The *acetate* **10** was obtained by treatment of **9** with pyridine and Ac_2O overnight at room temp. Crystallisation from light petroleum–acetone gave prisms m.p. 228–230°; λ_{max} 210 nm (ϵ = 6200); ν_{max} 1780, 1735, 1505 and 878 cm^{-1}; δ 1.01 (3 H, d, J = 7 Hz, *sec*-Me), 2.07 (3 H, s, OAc), 3.90 and 4.37 (1 H each, d of d, AB part of an ABX system, J_{AB} = 11.5, J_{AX} = 5.0, J_{BX} = 8.5 Hz, 2 H-18), 4.60 (1 H, m, $W_{1/2}$ = 6 Hz, H-3), 5.40 (1 H, t, J = 8.5 Hz, H-12), 6.43 and 7.48 (1 H and 2 H respectively, furan). (Found: C, 66.3: H, 6.2. M^+, *m/e* 402. $C_{22}H_{26}O_7$ requires: C, 65.7: H, 6.5%; *M*, 402).

The acid **11**. Jones reagent was added dropwise to a soln of **9** (22 mg) in acetone (10 ml) at room temp. The product (18 mg), isolated in the usual way, recrystallised from MeOH to give the *acid* **11** as prisms, m.p. 280° (dec); λ_{max} 209 nm (ϵ = 6600); ν_{max} 2700, 1770, 1715, 1506 and 875 cm^{-1}; δ (C_5D_5N) 1.07 (3 H, d, J = 7 Hz, *sec*-Me), 5.00 (1 H, d, J = 4 Hz, H-3), 5.54 (1 H, t, J = 8.5 Hz, H-12), 6.59, 7.70 and 7.83 (1 H each, furan), 9.36 (CO_2H). (Found: C, 64.9; H, 5.5. $C_{20}H_{22}O_7$ requires: C, 64.2; H, 5.9%).

The *methyl ester* **12**, obtained from the acid with diazomethane, crystallised as prisms from MeOH, m.p. 290° (dec). It had λ_{max} 210 nm (ϵ = 6000); ν_{max} 1770, 1740, 1504 and 876 cm^{-1}; δ 1.02 (3 H, d, J = 7 Hz, *sec*-Me), 3.73 (3 H, s, CO_2Me), 4.72 (1 H, m, $W_{1/2}$ = 6 Hz, H-3), 5.33 (1 H, t, J = 8 Hz, H-12), 6.33 and 7.38 (1 H and 2 H respectively, furan). [Found: M^+, *m/e*, 388.152. $C_{21}H_{24}O_7$ requires: *M*, 388.152].

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