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FURANOSESQUITERPENES FROM THE ESSENTIAL OIL OF MYRRH*

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Key Word Index—*Commiphora molmol*, Burseraceae, essential oil; myrrh, furanogermacranes, furanoguaiane, 1(10)*E*,4*E*-furanodiene-6-one, 1(10)*Z*,4*Z*-furanodiene-6-one, 2-methoxyfuranodiene, 2-acetoxyfuranodiene, 4,5-dihydrofuranodiene-6-one; 2-methoxyfuranoguaia-9-ene-8-one

Abstract—An examination of the essential oil of myrrh from *Commiphora molmol* has permitted the identification of 1(10)Z,4Z-furanodiene-6-one, 2-methoxyfuranodiene, 2-acetoxyfuranodiene, 4,5-dihydrofuranodiene-6-one and 2-methoxyfuranoguaia-9-ene-8-one.

INTRODUCTION

The essential oil of myrrh from *Commiphora molmol* is rich in furanosesquiterpenes [2]. Nine of them belong to the furanogermacrane group of compounds which have previously been isolated from plants of the Zingiberaceae and Lauraceae but not from the Burseraceae. Of the nine furanogermacranes only furanodiene [1(10)*E*,4*E*-furanodiene] and its 6-oxo derivative furanodienone were reported in the literature and we have already reported the identification of 2-methoxy-4,5-dihydrofuranodiene-6-one, 5-acetoxy-2-methoxy-4,5-dihydrofuranodiene-6-one and 3-methoxy-10-methylenefuranogermacra-1-ene-6-one [2]. In this paper we describe the isolation and the structural elucidation of the remaining four new furanogermacranes and a new furanoguaiane, also obtained from the essential oil of myrrh.

RESULTS AND DISCUSSION

In addition to 1(10)*E*,4*E*-furanodiene-6-one [3] the oil of myrrh contains its *cis*-isomer 1(10)*Z*,4*Z*-furanodiene-6-one (**1**), a colourless liquid with an intense fragrance. The two isomers were separated without difficulty. Compound **1** gave, like all other described furanosesquiterpenes, a positive Ehrlich colour test, indicating the presence of a furan ring Compound **1** had the molecular formula $C_{15}H_{18}O_2$, $[M]^+$ at *m/z* 230 and the mass spectrum was very similar to that of 1(10)*E*,4*E*-furanodiene-6-one The furan ring was also confirmed by the IR spectrum.

The ^{13}C NMR spectrum demonstrated that **1** had a germacrane skeleton. The chemical shifts in the broad band spin-decoupled spectrum, the multiplicities in the off-resonance spectrum and the assignment of the signals are shown in Table 1. The carbon bearing an oxygen function resonated at δ 193.2. Its position below δ 200 is caused by its olefinic conjugation [4–6]. The UV spectrum showed two maxima at 252 and 200 nm. These wavelengths were somewhat shorter than those of 1(10)*E*,4*E*-furanodiene-6-one, caused probably by the *cis*-configuration of the Δ^4-bond and the resulting disturbance of the conjugation with the furan system. The peaks of the mass spectrum, especially its base peak at *m/z* 122, resembled in their relative intensities the mass spectrum of authentic 1(10)*E*,4*E*-furanodienone [3].

The ^{1}H NMR spectrum indicated the presence of a β-substituted furan ring. The α-proton appeared as a broad singlet at δ 7.08. This chemical shift value excluded the C-9 position of the oxo group [7, 8]. Thus, only the C-6 position was concerned. The two olefinic protons at 5.88 (*s*) and 5.29 (*t*) were broadened by long range coupling. The singlet was due to H-5 and the triplet to H-1. Their *cis*-position to the corresponding methyl groups was confirmed by the intramolecular Nuclear–Overhauser effect. Upon irradiation at the signal of the C-15 methyl protons (δ 1.65) the intensity of the triplet at 5.29 (H-1) increased *ca* 24%. Irradiation at the signal of the C-14 methyl protons (δ 1.76) caused the intensity of the singlet to increase by *ca* 16%.

The crystalline 2-methoxyfuranodiene (**2**) had the molecular formula $C_{16}H_{22}O_2$, $[M]^+$ at *m/z* 246. The fragments arising by the retro-Diels–Alder cleavage (*m/z* 108 and 138) indicated that C-6 and C-9 were unsubstituted. The furanogermacrane skeleton was demonstrated by the ^{13}C NMR spectrum. The broad band spin-decoupled spectrum showed only 15 lines for 16 carbon atoms because two sp^2 hybridized carbon atoms had exactly the same chemical shift (Table 1). The two downfield signals at δ 79.3 (*d*) and 57.3 (*q*) were assigned to the carbons of the ether group [4, 9] and the quartet indicated it to be the methyl ether.

The ^{1}H NMR spectrum showed the α-furan proton at δ 7.07 (*br s*). The triplet at 5.05 was proved by spin decoupling to be due to the olefinic H-5, neighbouring to the C-6 methylene group (3.07, *d*, *J* = 7.5 Hz). The doublet at 4.99 (*J* = 10.5 Hz) was assigned by spin decoupling to the olefinic H-1. The doublet of triplets at 4.13 (J_1 = 10.5 Hz, J_2 = 4.5 Hz) was assigned to H-2 vicinally coupling with H-1 and the two protons at C-3. The downfield shift was caused by the inductive effect of the geminal methoxy group The protons of the ether methyl group appeared at 3.41 as a sharp singlet. The upfield shift of the methyl group to 1.36 can be ascribed to the diamagnetic shielding by the opposite double bond [10]. The spectroscopic data were in agreement with the structure **2**.

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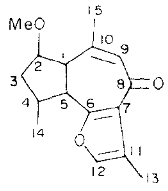
*This work is taken from the Ph D thesis of P N [1].



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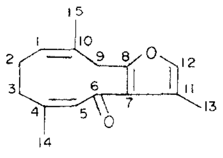

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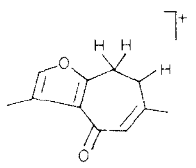

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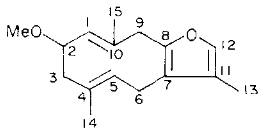

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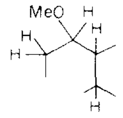

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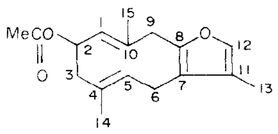

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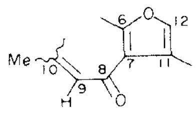

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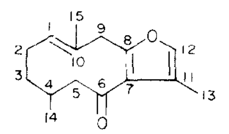

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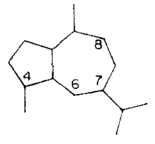

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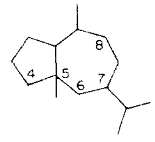

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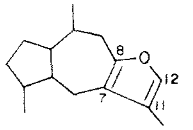

5f

Compound **2** was accompanied by the colourless wax **3** with the molecular formula $C_{17}H_{22}O_3$, $[M]^+$ at *m/z* 274. The base peak at *m/z* 43 $[MeC{\equiv}O]^+$ and the peak at *m/z* 214 $[M - MeCOOH]^+$ with 50 % relative intensity were typical for an acetyl ester [11]. The peak at *m/z* 108 indicated that, as in **2**, the β-methylated furan ring and also the neighbouring carbon atoms, C-6 and C-9, were unsubstituted.

The furanogermacrane skeleton was demonstrated by the ^{13}C NMR spectrum (Table 1). The signals at δ 170.7 (*s*, off-resonance spectrum) and 21.2 (*q*) were assigned to the carbonyl carbon atom and to the methyl group of the acetyl ester. According to the literature [12–14] the signals at 148.6 (*s*), 136.2 (*d*) and two singlets at 121.9 and 119.4 were characteristic of the furan carbon atoms. The β-methyl group of the furan ring resonated at δ 8.8 (*q*). The

Table 1 ^{13}C NMR spectral data of compounds **1–5** ($CDCl_3$, TMS as internal standard)

C No	**1** (62.89 MHz)	C No	**2** (22 64 MHz)	C No.	**3** (62 89 MHz)	C No	**4** (62 89 MHz)	C No	**5** (62 89 MHz)
1,5	129.0 *d*	1,5	131 1 *d*	1,10	130.6 *d*	1	130 2 *d*	1,5	59 7 *d*
	123.8 *d*	4,10	129 8 *s/d*		127.8 *d*	2,3,5	52.6 *t*		50 5 *d*
4,10	140.7 *s*		136 3 *s*	2	72.5 *d*		34.0 *t*	2	82 2 *d*
	133.9 *s*	2	79 3 *d*	3,6,9	45 0 *t*		26 0 *t*	3	38 1 *t*
2	36.2 *t*	3,6,9	46 1 *t*		40 8 *t*	4	28 7 *d*	4	30 2 *d*
3	26 0 *t*		41 1 *t*		24 4 *t*	6	201 9 *s*	6	147 6 *s*
6	193.2 *s*		24 5 *t*	4,5	136 0 *s*	7	126 1 *s*	7,11	140 8 *s*
7,11	122 8 *s*	7,11	121.8 *s*		129 2 *s*	8	151.6 *s*		122 6 *s*
	121 3 *s*		119.4 *s*	7,11	121 9 *s*	9	38.2 *t*	8	195 4 *s*
8	161 3 *s*	8	148 7 *s*		119.4 *s*	10	138.0 *s*	9	116 9 *d*
9	32.7 *t*	12	136 2 *d*	8	148 6 *s*	11	119 3 *s*	10	158 6 *s*
12	138.3 *d*	13	8 8 *q*	12	136 2 *d*	12	137 4 *d*	12	138 2 *d*
13	9 3 *q*	14,15	17 5 *q*	13	8 8 *q*	13	8 1 *q*	13	10 0 *q*
14	22 4 *q*		17 2 *q*	14,15	17 3 *q*	14	23 0 *q*	14,15	22 0 *q*
15	19 0 *q*	OMe	57 3 *q*		17 2 *q*	15	17 2 *q*		21 9 *q*
				$\mathrm{O{=}\underline{C}{-}OMe}$	170 7 *s*			–OMe	56 3 *q*
				$\mathrm{O{=}C{-}O\underline{Me}}$	21 2 *q*				

two quartets at 17.3 and 17 2 corresponded to the two vinylic methyl groups (C-14 and C-15). In the ^1H NMR spectrum of **3** the α-proton of the furan ring resonated at δ 7.07 (*br s*) and the β-methyl group was at 1.92 (*d*, $J = 1.2$ Hz). Two olefinic protons gave a triplet at 5.09 ($J = 7.5$ Hz) and a doublet at 5.04 ($J = 10.5$ Hz), respectively

By spin-decoupling experiments the signals at δ 5.09 (*t*) and 5.04 (*d*) could be assigned to the olefinic H-5 and H-1. The downfield shift of H-2 (5 53, *dt*), coupling with the olefinic H-1 and the two protons at C-3, was caused by the acetoxy group and confirmed its attachment at C-2 From all the spectral information it was concluded that **3** was 2-acetoxyfuranodiene, a compound which has not been described until now.

The fractions containing **1–3** were accompanied by a colourless oil, **4**. Its molecular formula $C_{15}H_{20}O_2$, with $[M]^+$ at m/z 232, was two mass units higher than that of **1** The base peak of **4** was at m/z 175 The fragment at m/z 122, the base peak in the mass spectrum of **1**, is one of the main peaks in the mass spectrum of **4** (relative intensity 39 %). This indicated an oxygen group at C-6 or C-9 The ^{13}C NMR spectrum, measured at 30°, showed some sharp signals and some which were broadened and very small The broadened lines suggest a conformational movement in the molecule [4, 5, 15, 16]. At a measuring temperature of 60° the broadened signals became sharper (Table 1) Sharp signals at low temperatures gave the four furan carbon atoms (δ 151.6, *s*; 137.4, *s*, 119.3, *s*; 126.1, *s*), the carbons of the trisubstituted double bond (138.0, *s*, 130.2, *d*), the three sp^3 hybridized carbon atoms of the β-methyl group at the furan ring (8.1, *q*), the methyl group at the double bond (17.2, *q*) and the methylene group between the double bond and the furan ring (38.2, *t*). This part of the molecule was not so flexible as the part between C-3 and C-7. The ^{13}C NMR spectrum demonstrated the germacrane skeleton for **4**.

The ^1H NMR spectrum showed the α-furan proton at δ 7.0. The shift indicated that there was no oxo group at C-9. A broad triplet at 5.37 ($J = 7.5$ Hz) was caused by an olefinic proton vicinally coupling with two methylene protons which resonated between 2 0 and 2.5. This was confirmed by spin-decoupling experiments. The broad singlet at 1.62 was characteristic for a vinylic methyl group. Besides the double bonds in the furan ring only one double bond could be present in the rest of the molecule Therefore, the second methyl group must be attached to a saturated carbon atom (δ 1.01, *d*, $J = 7$ Hz). To decide if the methylene group at C-5 or C-9 was in proximity to the oxo group a shift experiment with $Eu(fod)_3$ was performed In this experiment the doublet of doublets at δ 2 90 ($J_1 = 10$ Hz, $J_2 = 20$ Hz) shifted significantly downfield. Therefore, the doublet of doublets was established to be due to H-5a and H-5b which are near to the oxo group. Consequently, the isolated methylene group and the double bond were located at C-9 and C-1–C-10, respectively. The UV spectrum of **4** showed maxima at 211 and 262 nm; the latter proved the presence of an α,β-unsaturated oxo group. These results confirmed that **4** was 4,5-dihydrofuranodiene-6-one. Compound **4** is the fourth 4,5-dihydrofuranogermacrane derivative obtained from the essential oil of myrrh [2] This is the first time that this type of furanosesquiterpene has been isolated as a natural product.

From the fraction of the essential oil which contained **1** and **4** we isolated a further furanosesquiterpene (**5**) (3 %), which was a colourless liquid with an aromatic fragrance. Compound **5** had a molecular formula of $C_{16}H_{20}O_3$, $[M]^+$ at m/z 260, with the dominating base peak at m/z 175 None of the other peaks had a relative intensity exceeding 10 % By exact mass measurements the base peak had the molecular formula $C_{11}H_{11}O_2$, which agreed with the partial structure **5a**. The fragments at m/z 228 and 213 indicated the presence of a methoxy group with these ions originating by loss of a methanol unit from the molecular ion $[M]^+$ and $[M - Me]^+$, respectively. More information was provided by the 16 signals of the ^{13}C NMR spectrum (Table 1) The signal at δ 195 4 (*s* in the off-resonance spectrum) indicated the presence of a carbonyl group. By comparison with the resonance of a saturated ring ketone this carbonyl group must be conjugated The signals at 138.2 (*d*), 147.6 (*s*), 122.6 (*s*) and 140.8 (*s*) could be due to the furan carbon atoms A singlet (158 6) and a doublet (116 9) must be co-ordinated to a trisubstituted double bond independent from the furan ring. The signals at 82.2 (*d*) and 56.3 (*q*) indicated the presence of a methyl ether group. A quartet at 10.0 was assigned to the *β*-methyl group of the furan ring. The doublets (59.7 and 50.5) indicated a proton at each of the bridge-head carbon atoms and, therefore, angular methyl groups could be excluded. A third doublet (30.2) indicated a ring methylene carbon atom with a methyl group. All the ^{13}C NMR data indicated a tricyclic skeleton for **5**.

These results were confirmed by the ^{1}H NMR (500 MHz) spectrum. A peak at δ 7.04 (q, J = 1.2 Hz) was diagnostic for the *α*-proton of the furan ring. The *β*-methyl protons, which were in allylic coupling with this proton, were present at 2.23 (d, J = 1.2 Hz) and this was confirmed by a double resonance experiment. The doublet of quartets at δ 6.40 (J_1 = 1.5 Hz, J_2 = 2.5 Hz) for an olefinic proton indicated the allylic coupling with the protons of a vinylic methyl group. Its protons were present at δ 2.14 (t, J = 1.5 Hz) and this was confirmed by a spin-decoupling experiment. The deshielding of the olefinic proton and the absence of a vicinal coupling indicated that it was in the neighbourhood of a carbon bearing an oxygen function. This deduction was in agreement with the results of the ^{13}C NMR spectrum. The sharp singlet at 3.30 was due to the hydrogens of an ether methyl group. The hydrogen geminal to the methoxy group resonated as a doublet of quartets (4.00, J_1 = 6.5 Hz, J_2 = 0.6 Hz). The splitting indicated three neighbouring protons of a methylene and a methine group. Irradiation at 4.00 simplified the group of signals between 1.5 and 2.0. Irradiation at 1.7 transformed the doublet of quartets at 4.00 to a doublet of doublets. The third methyl group of the skeleton was secondary and characterized by a doublet of doublets at 1.08 (J_1 = 7.5 Hz, J_2 = 5.5 Hz). As demonstrated by a double resonance experiment the proton coupling with the protons of this methyl group resonated as a multiplet with a centre at 2.77. The results of the spin-decoupling experiment confirmed that the secondary methyl group and the methoxy group were not vicinally related to each other. Therefore, it was deduced that the bridge-head methine group was vicinal to the methyl ether group. The partial structure was, therefore, deduced to be **5b**.

The UV spectrum of **5** showed absorption maxima at δ 216, 239 (sh), 318 and 330 (sh) nm. The longwave maxima confirmed the $\alpha,\beta,\alpha',\beta'$-conjugation of the carbonyl system. Therefore, the oxo function was positioned between the double bond and the furan ring (C-8). This implied a further partial structure, **5c**.

The partial structures **5b** and **5c**, together with the information from the various spectra, showed that the structure was based on a five- and a seven-membered ring compound (e.g. guaiane, **5d**, or pseudoguaiane, **5e** condensed to a furan ring). As **5** contained a secondary methyl group it must be a guaiano derivative (methyl group at C-4). The furan ring built up from the isopropyl group (at C-7) of the guaiane skeleton could be established either by bonding to C-6 (**5**) or to C-8 (**5f**). Considering all the results the compound had to have the skeleton shown in **5**. Until now only gnididione [17] has been described which has a furanoguaiane skeleton as in **5**.

Assuming that partial structure **5f** would be the skeleton of **5** a long range coupling between H-9 and H-12 would then be expected in the ^{1}H NMR spectrum. However, both H-12 (*q*) and H-9 (*dq*) showed sharp signals. Upon irradiation at H-12 and H-9 no alteration was observed in the spectrum. Irradiation at the signal of the olefinic methyl group (δ 2.14) changed the triplet of the olefinic proton to a sharp doublet. This was caused by allylic coupling with the hydrogen of the bridge-head. All the results, therefore, indicated that **5** must be 2-methyoxy-furanoguaia-9-ene-8-one.

EXPERIMENTAL

Compounds **1–5** were isolated from the fractionated essential oil of myrrh as described in the previous publication [18].

1(10)Z,4Z-*Furanodiene-6-one* (**1**). Compound **1** (95 mg) was separated from curcerenone and **5** by CC on Si gel 60 (300 g, < 0.063 mm), developed with *n*-hexane–Et_2O (9:1) and *n*-hexane–Et_2O (4:1). Colourless liquid. RR_t (XE-60) 1.5, RR_t (capillary column) 1.43, R_f 0.18 (*n*-hexane–Et_2O, 9:1). IR ν_{max}^{film} cm^{-1}: 3030 (=CH), 2970, 2930, 2865, 1655 (C=O), 1533 (C=C, furan), 1450, 1440, 1403, 1380, 1155, 1105, 1018 (C–O–C, furan), 895, 845, 755. UV λ_{max}^{EtOH} nm: 252 (ε, 3100), 200. ^{1}H NMR (90 MHz, $CDCl_3$, TMS as int. standard): δ 7.08 (1H, *br s*, α-furan-H), 5.88 (1H, *br s*, H-5), 5.29 (1H, *t*, J = 7.5 Hz, H-1), 3.34 (2H, AB-system, δ_A = 3.61, δ_B = 3.06, J_{AB} = 15 Hz, H-9a, H-9b), 2.20 (3H, *d*, J = 1.5 Hz, methyl furan), 1.76 (3H, *d*, J = 1.5 Hz, vinyl methyl at C-4), 1.65 (3H, *br s*, vinyl methyl at C-10), 1.6–2.4 (4H, *m*, 2 × H-2, 2 × H-3). ^{13}C NMR: Table 1. MS (70 eV) m/z (rel. int.): 230 $[M]^+$ ($C_{15}H_{18}O_2$) (28), 215 (22), 150 (39), 123 (16), 122 (100), 94 (32), 91 (23), 81 (39), 79 (13), 77 (20), 65 (17), 53 (13), 41 (17), 39 (24). $C_{15}H_{18}O_2$ calc. 230.1307, found 230.1306 (MS). NOE: H-1–H-15 interaction, double-resonance frequency (a) 148.5 Hz, integrating signal of H-1 (δ 5.29), integrator curve increase 24% (averaged over several measurements); (b) double resonance frequency 158.0 Hz, integrating signal of H-15 (δ 5.88), integrator curve increase 16%.

2-*Methoxyfuranodiene* (**2**). Compound **2** (112 mg) was separated from the accompanying furanoeudesma-1,4-diene-6-one [18] by CC on $AgNO_3$ (10%)–Si gel-60 (80 g, 0.06–0.2 mm) developed with *n*-hexane–Et_2O (7:3) and *n*-hexane–Et_2O (3:2). Colourless needles, mp 58–59°. RR_t (capillary column) 1.57, R_f 0.59 (*n*-hexane–Et_2O, 7:3). IR ν_{max}^{KBr} cm^{-1}: 2990, 2980, 2950, 2930, 2905, 2870, 2830, 1660 (C=C), 1615 and 1555 (C=C, furan), 1445, 1430, 1390, 1375, 1190, 1153, 1140, 1115, 1095 (C–O–C, methyl ether), 965, 808, 790, 768. UV λ_{max}^{EtOH} nm: 208 (ε, 10800). ^{1}H NMR (90 MHz, $CDCl_3$, TMS as int. standard): δ 7.07 (1H, *br s*, α-furan-H), 5.05 (1H, *t*, J = 7.5 Hz, H-5), 4.99 (1H, *d*, J = 10.5 Hz, H-1), 4.13 (1H, *dt*, J_1 = 10.5 Hz, J_2 = 4.5 Hz, H-2), 3.52 (2H, *br s*, 2 × H-9), 3.41 (3H, *s*, OMe), 3.07 (2H, *d*, J = 7.5 Hz, 2 × H-6), 2.51 (2H, *dd*, J_1 = 10.5 Hz, J_2 = 4.5 Hz, 2 × H-3), 1.92 (3H, *d*, J = 1.2 Hz, methyl furan), 1.64 (3H, *br s*, vinyl methyl at C-4), 1.36 (3H, *br s*, vinyl methyl at C-10). ^{13}C NMR: Table 1. MS (70 eV) m/z (rel. int.): 246 $[M]^+$ ($C_{16}H_{22}O_2$) (20), 214 (11), 159 (32), 138 (10), 123 (30), 119 (10), 108 (14), 107 (14), 105 (14), 91 (22), 85 (23), 79 (14), 77 (15), 55 (13), 53 (12), 45 (100), 43 (11), 41 (20), 39 (13), 32 (10). $C_{16}H_{22}O_2$ calc. 246.1620, found 246.1615 (MS).

2-*Acetoxyfuranodiene* (**3**). Compound **3** (15 mg) was separated from an accompanying unidentified furanosesquiterpene ketone by CC on $AgNO_3$ (10%)–Si gel (80 g, 0.06–0.2 mm), developed with *n*-hexane–Et_2O (1:1). Colourless wax. RR_t (capillary column) 2.0, R_f 0.67 (*n*-hexane–Et_2O, 1:1). IR ν_{max}^{film} cm^{-1}: 2930, 2870, 2835, 1735 (C=O, ester), 1600, 1550 (C=C, furan), 1450, 1435, 1375, 1365, 1240 (C–O–C, ester), 1140, 1023 (C–O–C, furan), 985, 965, 765. ^{1}H NMR (90 MHz, $CDCl_3$, TMS as int. standard): δ 7.07 (1H, *br s*, α-furan-H), 5.53 (1H, *dt*, J_1 = 10.5 Hz, J_2 = 4.5 Hz, H-2), 5.09 (1H, *t*, J = 7.5 Hz, H-5), 5.04 (1H, *d*, J = 10.5 Hz, H-1), 3.50 (2H, *br s*, 2 × H-9), 3.08 (2H, *d*, J = 7.5 Hz, 2 × H-6), 2.52 (2H, *dd*, J_1 = 10.5 Hz, J_2 = 4.5 Hz, 2 × H-3), 2.06 (3H, *s*, –OCOMe), 1.92 (3H, *d*, *J* = 1.2 Hz, methyl furan), 1.67 (3H, *br s*, vinyl methyl at C-4), 1.41 (3H, *br s*, vinyl methyl at C-10) ^{13}C NMR Table 1. MS (70 eV) *m/z* (rel int) 274 $[M]^+$ ($C_{17}H_{22}O_3$) (10), 214 (50), 119 (44), 149 (23), 147 (29), 146 (28), 135 (39), 119 (24), 109 (41), 108 (67), 106 (39), 105 (24), 91 (37), 79 (27), 77 (22), 43 (100), 41 (28) $C_{17}H_{22}O_3$, calc. 274.1569, found 272.1577 (MS)

4,5-*Dihydrofuranodiene*-6-*one* (**4**) Compound **4** (85 mg) was separated by CC on $AgNO_3$ (10%)–Si gel (20 g 0.06–0.2 mm) developed with *n*-hexane–Et_2O (4:1) Colourless liquid *RR*$_t$ (capillary column) 1.28, R_f 0.63 (*n*-hexane–Et_2O, 4:1) IR $\nu_{\max}^{\text{film}}$ cm^{-1}. 2955, 2930, 2870, 1690 (C=O), 1610 and 1555 (C=C, furan), 1455, 1435, 1410, 1390, 1375, 985, 915, 750 UV $\lambda_{\max}^{\text{EtOH}}$ nm 262 (ε, 1000), 211 (10 600) ^{1}H NMR (90 MHz, $CDCl_3$, TMS as int standard) δ 7.00 (1H, *br s*, α-furan-H), 5.37 (1H, *t*, *J* = 7.5 Hz, H-1), 3.31 (2H, AB-system, δ_A 3.44, δ_B 3.17, J_{AB} = 16.5 Hz, H-9a, H-9b), 2.90 (2H, *dd*, J_1 = 10 Hz, J_2 = 20 Hz, H-5a, H-5b), 2.0–2.5 (5H, *m*, 2 × H-2, 2 × H-3), 1.89 (3H, *d*, *J* = 1.5 Hz, methyl furan), 1.62 (3H, *br s*, vinyl methyl at C-10), 1.01 (3H, *d*, *J* = 7 Hz, methyl at C-4) ^{13}C NMR Table 1 MS (70 eV) *m/z* (rel. int.). 232 $[M]^+$ ($C_{15}H_{20}O_2$) (67), 214 (26), 189 (24), 176 (28), 175 (100), 162 (44), 161 (48), 159 (25), 150 (22), 149 (31), 135 (20), 122 (39), 119 (22), 105 (22), 94 (27), 93 (23), 91 (37), 79 (20), 77 (31), 65 (27), 53 (20), 43 (23), 41 (46), 39 (35) $C_{15}H_{20}O_2$ calc 232.1463, found 232.1445 (MS).

2-*Methoxyfuranoguaia*-9-*ene*-8-*one* (**5**) Compound **5** (80 mg) was separated from **1** as described above Colourless oil, *RR*$_t$ (capillary column) 1.93, R_f 0.15 (*n*-hexane–Et_2O, 9:1) IR $\nu_{\max}^{\text{film}}$ cm^{-1} 3030 (=CH), 2960, 2930, 2870, 2830, 1665 (C=O), 1645 (C=C), 1595, 1570, 1535 (C=C, furan), 1455, 1410, 1385, 1375, 1275, 1110, (C–O–C, methyl ether), 1050 (C–O–C, furan), 1005, 995, 945, 840, 780, 770 UV $\lambda_{\max}^{\text{EtOH}}$ nm. 330 (sh, ε, 3100), 318 (3700), 239 (5100), 216 nm (13 600) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (1H, *q*, *J* = 1.2 Hz, α-furan-H), 6.40 (1H, *dq*, J_1 = 1.5 Hz, J_2 = 2.5 Hz, H-9), 4.00 (1H, *dq*, J_1 = 6.5 Hz, J_2 = 0.6 Hz, H-2), 3.30 (3H, *s*, –OMe), 2.77 (*m*), 2.23 (3H, *d*, *J* = 1.2 Hz, methyl furan), 2.14 (3H, *t*, *J* = 1.5 Hz, vinyl methyl at C-10), 1.82 (*m*), 1.7–1.5 (*m*), 1.08 (3H, *dd*, J_1 = 7.5 Hz, J_2 = 5.5 Hz, methyl at C-4) ^{13}C NMR Table 1. MS (70 eV) *m/z* (rel int) 260 $[M]^+$ ($C_{16}H_{20}O_3$) (10), 213 (6), 176 (10), 175 (100), 174 (6), 115 (4.5), 91 (5) $C_{16}H_{20}O_3$ calc 260.1412, found 260.1428 (MS), $C_{11}H_{11}O_2$ (base peak) calc. 175.0759, found 175.0833 (MS)

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