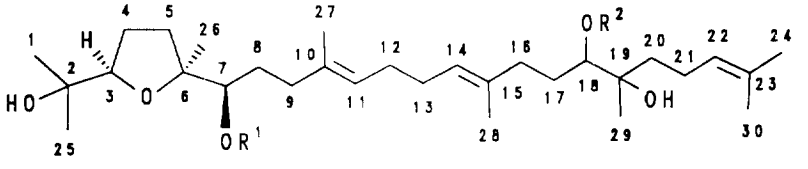
the ^{1}H NMR spectrum the oxymethine signals were split into a 3:2 ratio; the C-3 proton had resonances at δ 3.82 (t, J=7.3 Hz) and δ 3.83 (t, J=7.3 Hz), the C-7 proton at δ 3.58 (dd, J=10.3, 1.8 Hz) and δ 3.56 (dd, J=10.3, 1.8 Hz), and the C-18 proton at δ 3.36 (dd, J=10.6, 2.7 Hz) and δ 3.37 (dd, J=10.6, 2.7 Hz). In the ^{13}C NMR spectrum, C-3 had one resonance at δ 84.4 but C-6 had two resonances at δ 86.3 and 86.4. The methyl at C-6 gave cross-peaks with both the C-3 and C-7 protons in a NOESY spectrum; these correlations have also been observed in related compounds with the same relative stereochemistry at C-3, C-6 and C-7 as determined by X-ray analysis.[4,5] However, no attempt was made to determine the absolute stereochemistry of these compounds by the Mosher ester analysis since they showed signs of decomposition on standing.

When **1** was treated with acetic anhydride/pyridine the diacetate **1a** was formed; the signals did not show any doubling in CD_3OD, $CDCl_3$ or benzene-d_6. The C-3 proton in **1a** shifted upfield to δ 3.75 (dd, J=8.5, 6.6 Hz) while the C-7 and C-18 protons shifted downfield to δ 4.94 (dd, J= 10.4, 2.4 Hz) and δ 4.85 (dd, J=10.1, 2.7 Hz), respectively. These observations suggest that **1** adopts two different conformations in $CDCl_3$ but only one in CD_3OD. One conformation may involve intramolecular H-bonding that is present in $CDCl_3$ but not in hydrogen bonding solvents such as CD_3OD or when hydroxyl groups are acetylated. The alternative explanation of two stereoisomers seems very improbable since this would require both stereoisomers to have identical ^{1}H and ^{13}C NMR spectra in CD_3OD and on acetylation.



1 $R^1 = R^2 = H$; **1a** $R^1 = R^2 = Ac$; **2** $R^1 = H$, $R^2 = Ac$

Quassiol B (**2**), $C_{32}H_{56}O_6$, was isolated as a colorless gum, $[\alpha]_D$ +4.9° (c 0.6, $CHCl_3$), and had IR absorptions characteristic of hydroxyl (3500 cm^{-1}) and ester (1730 cm^{-1}) functionalities. The ^{1}H NMR spectrum of **2** was similar to that of **1** except that there were no doubling of the signals in $CDCl_3$, CD_3OD or benzene-d_6. The major differences were the downfield shift of an oxymethine signal from δ 3.36/3.37 in **1** to δ 4.84 (dd, J=10.6, 2.7 Hz) in **2** along with the appearance of an

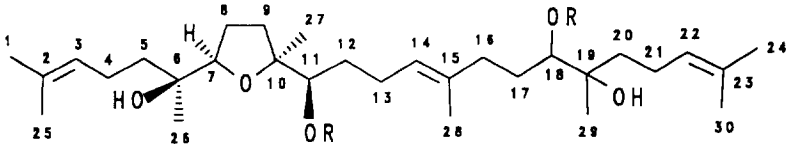
Table 2. ^{13}C NMR Assignments for Quassiols A (**1**), A Diacetate (**1a**), B (**2**), C Diacetate (**3a**), and D Diacetate (**4a**) in $CDCl_3$ at 100 MHz.[a]

Position	1	1a	2	3a	Eurylene[b]	4a
1	27.6	27.1	27.6	25.7	25.7*	25.7
2	72.0	71.0	72.0	131.5	131.6	132.1
3	84.4	84.8	84.4	124.6	124.5	124.2
4	28.0	26.2	26.9	21.9	22.1	22.1
5	31.2	33.8	31.3	37.7	37.6	37.7
6	86.3, 86.4	84.2	86.3	72.6	72.7*	74.2
7	76.7, 76.3	77.2	76.5	83.8	83.8*	79.1
8	30.2, 30.1	28.4	30.3	25.6	25.6*	26.6
9	36.7, 36.4	35.8	36.6	34.3	34.2*	36.2
10	135.1, 135.2	134.3	134.9	84.2	84.6*	134.3
11	124.8, 125.5	124.8	124.9	77.0	77.2*	124.8
12	28.0	27.9	28.2	29.8	27.1	28.2
13	28.0	27.9	28.1	24.1	26.9	28.2
14	125.0	124.9	124.8	124.6	78.2*	124.8
15	135.3, 135.2	134.4	134.3	134.7	86.6*	134.3
16	36.9, 36.7	36.0	36.2	35.9	34.9*	36.2
17	29.3, 29.1	27.4	27.6	27.0	25.8*	26.6
18	78.2, 78.0	79.0	79.2	78.5	83.6*	79.1
19	74.7, 74.6	74.0	74.2	73.8	72.0*	74.2
20	35.8, 35.7	37.5	37.7	38.0	37.3	37.7
21	22.1	21.8	21.1	22.2	22.1	22.1
22	124.7	124.3	124.2	124.5	124.5	124.2
23	131.7	132.0	132.0	131.7	131.6	132.1
24	25.7	25.5	25.7	25.7	25.7*	25.7
25	25.3, 25.1	24.1	25.3	17.6	17.6*	17.7
26	23.8, 23.7	22.6	23.7	24.1	24.2	23.6
27	16.1	15.8	16.0	22.5	22.5	16.1
28	16.0	15.8	16.1	15.8	22.8	16.1
29	23.3	23.3	23.5	22.4	24.0	23.6
30	17.7	17.4	17.7	17.6	17.6*	17.7
7-Ac	- -	171.1	- -	- -	- -	171.1
	- -	21.0	- -	- -	- -	21.1
11-Ac	- -	- -	- -	171.1	- -	- -
	- -	- -	- -	21.2	- -	- -
18-Ac	- -	171.3	171.1	173.3	- -	171.1
	- -	20.9	22.1	21.1	- -	21.1

[a]Assignments based on HMQC and HMBC experiments. [b]Data taken from reference 4.

acetate methyl singlet at δ 2.10. The THF proton at C-3 had a signal at δ 3.82 (t, J=7.3 Hz) while the C-7 proton resonated at δ 3.56 (dd, J=10.3, 1.8 Hz). The location of the acetate group in **2** was determined by an HMBC experiment which showed that the acetyl carbonyl at δ 171.1 and C-19 at δ 73.8 showed long-range correlations with the C-18 proton at δ 4.84. When compound **2** was acetylated, it gave the same diacetate **1a** that was formed on acetylation of **1**.

Quassiol C (**3**) was not obtained pure and was purified as the diacetate (**3a**). The ^{1}H NMR spectrum had signals due to three quaternary and five olefinic methyls, in addition to three oxymethine protons at δ 3.75 (dd, J=9.7, 7.3 Hz, C_7-H), δ 5.02 (dd, J=10.6, 2.4 Hz, C_{11}-H), and δ 4.87 (dd, J=10.4, 1.9 Hz, C_{18}-H). The presence of ^{13}C NMR signals at δ 83.8 (d) and δ 84.2 (s) in addition to the five olefinic methyls suggested that an internal THF system was present in **3a**. The position of the THF group was determined on the basis of a careful analysis of DQF-COSY and

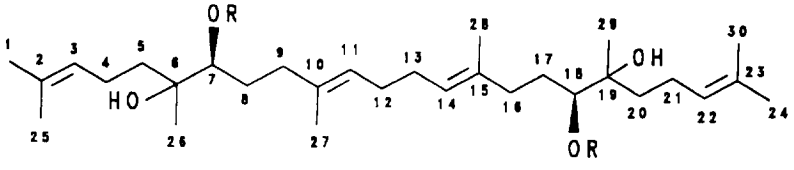


3 R = H; **3a** R = Ac

HMBC spectra to be at C-6/C-11. Compound **3** showed the same NOESY relationships and had almost identical ^{1}H and ^{13}C resonances as the right hand segment of the related eurylene, whose structure was determined by X-ray analysis.[4] However, at least sixteen of the carbon resonances reported[4] for eurylene were mis-assigned and a revised listing is included in Table 3; the reassigned carbons are marked with an asterisk. A stereoisomer of **3** as the 6,18,19-tri-*O*-MOM derivative, was recently synthesized as an intermediate in the total synthesis of teurilene.[22,23]

Quassiol D (**4**) was purified as the diacetate (**4a**), $C_{34}H_{58}O_6$, $[\alpha]_D$ +3° (*c* 0.40, $CHCl_3$). The ^{13}C NMR spectrum of **4a** had resonances for only seventeen carbons and this, along with the optical activity, suggested that the chiral centers at C-6 and C-7 were configurationally identical to those at C-19 and C-18, respectively. In addition, an examination of both its ^{1}H and ^{13}C NMR spectra revealed that it possessed four sp^3 carbons bearing oxygen and four double bonds, but did not contain a THF moiety. The locations of the oxygenated carbons were determined from DQF-COSY, HMQC and HMBC experiments. Compound **4** or a stereoisomer was recently synthesized as the 6,7,19-tri-

O-MOM ether and used in the total synthesis of teurilene;[22-24] it is the logical precursor to the more complex derivatives. The number of squalene triterpenes being reported in the literature is growing and were isolated mainly from marine algae belonging to the genus *Laurencia* and from plants from the Simaroubaceae and Meliaceae families.[3-11]



4 R = H; **4a** R = Ac

EXPERIMENTAL

The plant material was collected at the Goethe Creek, Essequibo, in November, 1987. Voucher specimens (CAP 334) were deposited at the Jenman's Herbarium, University of Guyana.

IR spectra were obtained on a Nicolet 3DX FTIR spectrometer. A Perkin-Elmer 243B polarimeter was used to obtain optical rotations. NMR spectra were recorded on a Varian XL-400 or a Varian Unity 500 spectrometer with TMS as the internal standard. A VG-70-250S mass spectrometer was used to obtain MS data.

General Extraction Procedure:

The dried, ground roots (6.54 kg) were extracted with 95% EtOH (93.5 liters). The extract was concentrated to a small volume (0.5 liters), defatted with hexane (5 x 200 mL), and subsequently extracted with CH_2Cl_2 to give brown viscous syrup (167 g) on removal of the solvent. This material, in portions, was chromatograhed on silica gel using CH_2Cl_2 with increasing amounts of MeOH as solvent system to give eight major fractions. Fraction 3 was rechromatographed on silica gel using hexane/acetone as mobile phase to give **1** (383 mg), **2** (131 mg) and impure **3** (43 mg) and **4** (178 mg) as judged by ^{1}H NMR. The latter two compounds were separately acetylated and purified by preparative TLC to give the diacetates **3a** and **4a**. Compound **2** (45 mg) was acetylated overnight with pyridine/acetic anhydride (0.5 ml each) to give compound **1a** (39 mg) after preparative TLC.

Quassiol A (**1**): Colorless gum; $[\alpha]_D$ -9.8° (*c* 0.41, $CHCl_3$); IR 3440, 1077 cm^{-1}; EIMS *m/z* 494 (M^+, 2%), 476(6), 461(8), 417(15), 349(66), 307(46), 143(100), 109(33), 69(55); *Exact mass* 494.3925 calcd for $C_{30}H_{54}O_5$ 494.3971.

Quassiol A diacetate (**1a**): Colorless gum; $[\alpha]_D$ -3.3° (*c* 0.15, $CHCl_3$); IR 3500, 1730 cm^{-1}; EIMS *m/z* 560 (M^+-H_2O, 13%), 544(27), 500(8), 484(20), 440(8), 257(12), 203(26), 135(65), 109(64), 69(100); *Exact mass* 560.4038 calcd for $C_{34}H_{58}O_7$ (*M*-H_2O) 560.4078.

Quassiol B (**2**): Colorless gum $[\alpha]_D$ +4.9° (*c* 0.60, $CHCl_3$); IR 3440, 1729 cm^{-1}; EIMS *m/z* 536 (M^+, 1%), 518(2), 458(2), 393(7), 375(26), 333(16), 203(7), 143(100), 109(31), 69(45); *Exact mass* 536.4090 calcd for $C_{32}H_{56}O_6$ 536.4077.

Quassiol C diacetate (**3a**): Colorless gum; $[\alpha]_D$ +6.1° (*c* 0.18, $CHCl_3$); IR 3500, 1730 cm^{-1}; EIMS *m/z* 578 (M^+, 2%), 560(16), 491(13), 434(24), 375(25), 211(36), 135(44), 109(65), 69(100); *Exact mass* 578.4180 calcd for $C_{34}H_{58}O_7$ 578.4182.

Quassiol D diacetate (**4a**): Colorless gum; $[\alpha]_D$ +3.0° (*c* 0.40, $CHCl_3$); IR 3450, 1730 cm^{-1}; EIMS *m/z* 562 (M^+, 0.5%), 544(15), 529(17), 484(12), 451(22), 263(29), 203(52), 109(86), 69(100); *Exact mass* 562.4198 calcd for $C_{34}H_{58}O_6$ 562.4233.

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Structural and Solvent Effects upon Decarboxylation of 2,6-Disubstituted Benzoyloxyl Radicals. A Laser Flash Photolysis Study of Bis(2,6-disubstituted-benzoyl) Peroxides

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Abstract: The rate constants for decarboxylation of 2,6-dimethylbenzoyloxyl, 2,4,6-trimethylbenzoyloxyl and 2,6-dichlorobenzoyloxyl radicals are larger than those of benzoyloxyl, 4-methylbenzoyloxyl and 2-chlorobenzoyloxyl radicals, respectively, in carbon tetrachloride and acetonitrile; however, the values in the former solvent are significantly larger than those in the latter. The rate acceleration with the ortho substituents is ascribed to a nonplanar geometry of the radicals brought about by twisting of the carbonyloxyl group due to a steric effect of the substituents. The polar solvent serves to stabilize a twisted charge-transfer structure of the radicals and retards their decarboxylation.

INTRODUCTION

Aroyloxyl radicals such as benzoyloxyl radicals are generated from thermolysis or photolysis of the parent diaroyl peroxides, which are widely used to initiate free-radical chain reactions in solution.[1-4] Kinetic studies on the aroyloxyl radicals have been made by means of product analysis,[5-7] spin trapping,[8] CIDNP[9-11] and EPR.[12-14] However, applications of direct methods started very recently with time-resolved EPR (TREPR)[15,16] and laser flash photolysis (LFP).[17-24] The results on decarboxylation of the aroyloxyl radicals have been explained in terms of a coplanar arrangement of the aromatic ring and carbonyloxyl group[17-19,24] though theoretical studies have presented no strong preference for the aroyloxyl radicals of a planar or perpendicular structure.[7,14,25-27]

In order to get further insight into structure-reactivity relationships of the aroyloxyl radicals, we prepared and photolyzed various bis(2-substituted-benzoyl)[23,28] and bis(2,6-disubstituted-benzoyl) peroxides[29] with 308-nm laser pulses, and monitored their transient absorption spectra. A single ortho-substituent such as a chlorine atom and a methoxyl group exhibited no structural effects upon behavior of the benzoyloxyl radicals compared with the corresponding 4-substituted species; the carbonyloxyl moiety remains in the plane of the aromatic ring. An EPR study of 2-chlorobenzoyloxyl radicals suggested that the ground state of the radical takes an almost planar structure,[30] whereas a 2-bromo substituent resulted in a twisted geometry of the corresponding benzoyloxyl radical.[31]

The introduction of an alkyl or aralkyl group such as methyl, ethyl and benzyl groups in the ortho position of the phenyl ring decreased the lifetime of the benzoyloxyl radicals.[23,28] This was due to the fast intramolecular hydrogen-atom transfer in the 2-alkylbenzoyloxyl or 2-aralkylbenzoyloxyl radicals through a planar six-membered ring transition state.

On the contrary, the introduction of substituents such as chlorine atoms and methyl groups in both of the 2- and 6-positions brought about a dramatic change in behavior of the benzoyloxyl radicals. In a preliminary communication,[29] we reported the behavior of 2,6-disubstituted benzoyloxyl radicals in acetonitrile. 2,6-Dimethylbenzoyloxyl radicals did not undergo intramolecular hydrogen-atom transfer but underwent decarboxylation, and the lifetimes of 2,6-dimethylbenzoyloxyl, 2,4,6-trimethylbenzoyloxyl and 2,6-dichlorobenzoyloxyl radicals were shorter than those of benzoyloxyl, 4-methylbenzoyloxyl and 2-chlorobenzoyloxyl radicals, respectively. In this paper, we report a full account of our work on these radicals in acetonitrile and carbon tetrachloride, and discuss the effects of ortho substituents upon the structure and reactivity of the benzoyloxyl radicals.

RESULTS

Transient Absorption Spectra. Bis(2,6-dimethybenzoyl) peroxide (2,6-Me_2BPO, 5×10^{-3} mol dm^{-3}) was photolyzed with 308-nm laser pulses in acetonitrile or carbon tetrachloride under argon at room temperature.[28] The transient absorption spectra observed in acetonitrile are shown in Figure 1 together with a decay profile of the absorption monitored at 780 nm. The broad structureless band with a maximum around 700 nm is ascribable to 2,6-dimethylbenzoyloxyl radicals (2,6-$Me_2C_6H_3CO_2$·), as reported for various analogues.[17-24] However, no absorption bands ascribable to the benzylic radicals resulting from intramolecular hydrogen-atom transfer were observed in the 300–400-nm region[23,28] at room temperature and even at –40 °C in a higher concentration of 2,6-Me_2BPO (1×10^{-2} mol dm^{-3}; Figure 2). The time profile of the transient absorption monitored at 700 nm fits a single-exponential decay with a rate constant (k) of $(2.5\pm0.8)\times10^7$ s^{-1} at 20 °C. The rate constant was independent of the peroxide concentration in the range of 10^{-3}–10^{-2} mol dm^{-3}.

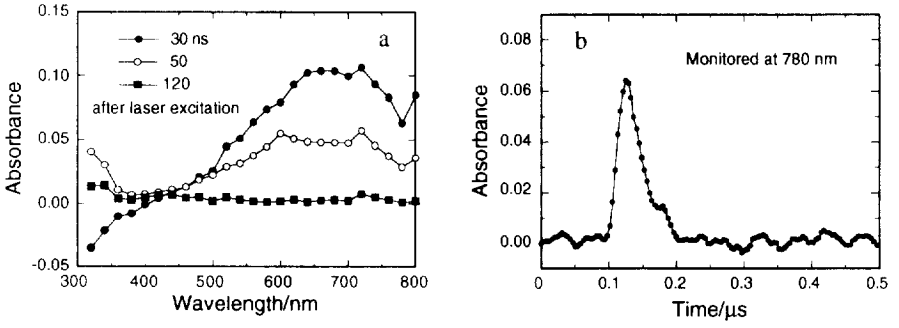

Figure 1. (a) Transient absorption spectra observed upon the 308-nm pulsed-laser excitation of 2,6-Me_2BPO in acetonitrile under argon at 23 °C, and (b) its decay profile monitored at 780 nm.