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DIHYDROMAMMEA C/OB: A NEW COUMARIN FROM THE SEED OF *MAMMEA AFRICANA*

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Key Word Index—*Mammea africana*; Guttiferae; 4-*n*-pentyldihydrocoumarins; 4-*n*-pentylcoumarins; 4-*n*-propylcoumarins; 4-phenylcoumarins; structure elucidation; ^{13}C NMR; biological significance.

Abstract—In addition to four known coumarins and the sterol friedelone, *Mammea africana* has yielded the novel dihydrocoumarin dihydromammea C/OB (8-(2-methylbuteryl)-5,7-dihydroxy-4-*n*-pentyl-3,4-dihydrocoumarin). This compound was identified by the interpretation of spectral data and comparison with other mammea coumarins and model compounds. The value of ^{13}C NMR in the structure elucidation of mammea coumarins and the biological significance of the findings are discussed.

INTRODUCTION

Mammea africana Sabine (Guttiferae) is a large evergreen tree found throughout the tropical rain forest zone of Africa [1]. Previous detailed chemical studies on both the seeds and bark have revealed the presence of a large number of 4-aryl and 4-alkyl-5,7-dihydroxycoumarins [2–4], almost invariably substituted at C-6 and C-8 by a variety of isoprene type side-chains. In complete contrast, the wood of this species contains a range of xanthones [5] typical of the Guttiferae [6].

Comparable studies on the seed of the New World species *M. americana* L. have shown it to contain a very similar group of coumarins [3, 7, 8]. Several of the 4-*n*-propylcoumarins isolated from *M. americana* have been shown to possess considerable insecticidal activity [8].

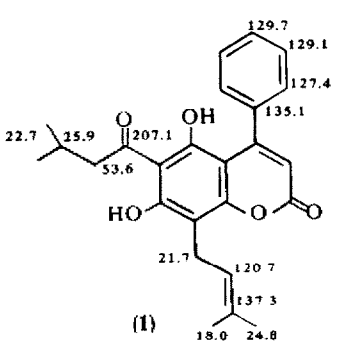
As part of a comparative study of the chemistry of a number of sympatric Guttiferae from west Cameroon, we wish to report the results of a re-examination of the bark and seed and an initial examination of the leaf.

RESULTS

From the bark, two known coumarins, mammea A/AA (**1**) and mammea B/BA (**2a**), were isolated and identified by comparison with spectral data previously recorded for them. The former has already been reported from both bark and seed, the latter only from the seed. Mammea A/AA was obtained in a yield in excess of 1% of the weight of the bark which is over three times the quantity recorded previously for the total coumarins of the bark. In addition to the two isolated compounds there was considerable ^{1}H NMR and MS evidence for the occurrence of mammea B/AB (**2b**) but this could not be isolated.

In contrast to the bark, the leaf contained only traces of phenolic compounds. From the petrol extract, a small amount of the sterol friedelan-3-one (**3**) was obtained. This compound was previously reported from *M. americana* seed by Crombie and Games [3] but had not been isolated from *M. africana*.

From a petrol extract of the seed, a number of coumarins were isolated by column chromatography over silica gel, eluting with petrol containing increasing amounts of ethyl acetate. Four separate bands were collected and the first three identified, on the basis of spectral data, as mammea C/BB (**4**), mammea A/AA (**1**) and a mixture of mammea B/BB (**2c**) and the isomeric mammea B/BA (**2a**). The mixture was resolved by repeated recrystallization from hexane to give pure mammea B/BA. Coumarins **1**, **2a** and **2c** have already



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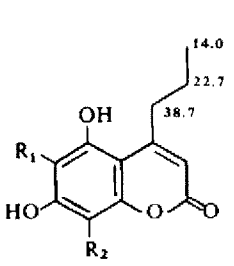

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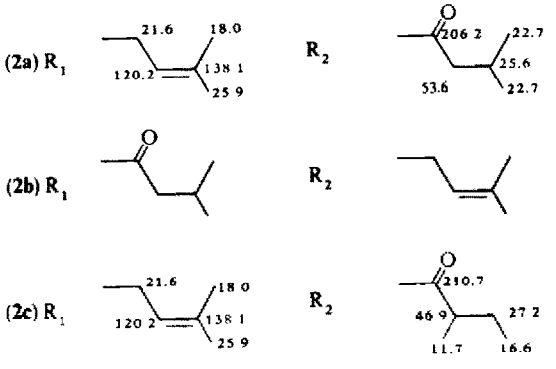

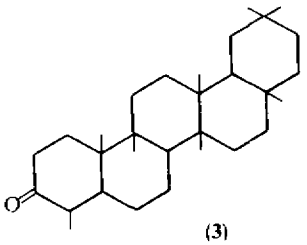

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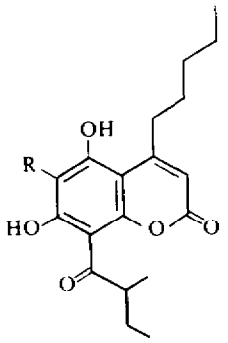
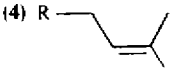


(4) R = 

(5) R = H

been reported from *M. africana* seed but **4** was known previously only from *M. americana* seed.

The final eluant from the column yielded an optically active solid, mp 125°, $C_{19}H_{26}O_5$. The UV spectrum underwent a bathochromic shift on the addition of NaOH typical of all 5,7-dihydroxycoumarins but differed from the others in that it exhibited only a vestigial long wavelength band. The IR spectrum exhibited typical bands at 3500 cm^{-1} for phenolic hydroxyl groups and 1650 cm^{-1} for the carbonyl of a buteryl side-chain. However the normal 1720–1740 cm^{-1} coumarin lactone carbonyl band was absent, being replaced by absorption at 1780 cm^{-1}. Carbonyl absorption at such a high wavelength suggested a saturated lactone rather than the normal α,β unsaturated system [9], an hypothesis confirmed by the similar bands observed in the model dihydrocoumarins **6** and **7**.

The simple MS fragmentation, showing loss of C_4H_9 to give a base peak at *m/e* 277 ($C_{15}H_{17}O_5$), confirmed the presence of the buteryl side-chain [2]. Further fragmentation was reminiscent of, but not identical with, that observed in the unusual mammea C/OB (**5**) from the bark of this species [2].

The PMR spectrum resolved all 26 protons and permitted a tentative structure to be formulated. The presence of two hydroxyls was confirmed by signals at δ 13.69 (1H) and 6.90 (1H). The considerable difference in resonance positions indicated that one of the hydroxyl groups (that at δ 13.69) was hydrogen bonded to a buteryl side-chain whilst the other was free. This observation permits the side-chain to be assigned to C-8 rather than C-6. For the side-chain a single deshielded proton forming a sextuplet (δ 3.71) and two methyl groups observed at δ 1.15 (doublet) and 0.95 (triplet) indicated the 2-methylbuteryl moiety previously encountered in mammea B/BB (**2c**).

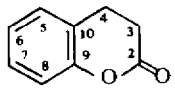
The single aromatic proton appeared at δ 6.31, *ca* 0.3 ppm lower than the resonance for the C-3 proton of typical mammae coumarins but in close agreement with recorded data for the C-6 proton of **5**. Assignment of the aromatic proton to C-6 completes the substitution of the benzene ring leaving the remaining 14 protons to be distributed on the lactone. The presence of a multiplet centred at δ 2.80 (2H) and a multiplet at δ 3.32 (1H) was in agreement with resonances observed for the C-3 and C-4 protons of **7** indicating the lactone ring was O—CO—CH_2—CH(R)—. The obvious inference that the remaining 11 protons and 5 carbons made up an *n*-pentyl side-chain was confirmed by ill-defined methylene resonance between δ 1.3 and 1.7 and a methyl resonance at δ 0.90.

The new coumarin must therefore have structure **8** and becomes the first complex dihydrocoumarin to have been isolated from *Mammea*. It has been assigned the trivial name dihydromammea C/OB, in line with previous nomenclature for this group of compounds.

^{13}C *NMR*

^{13}C NMR spectra of mammea coumarins have not previously been reported. An examination of the carbon shifts observed for **1**, **2a** **2c** and **8**, and for the synthetic dihydrocoumarins **6** and **7**, both confirmed the structure assigned to **8** and suggested that ^{13}C NMR could have considerable value with this type of compound. Assignments were made by analogy with published carbon shifts for coumarins [10], 4-phenylcoumarins [11], and on other systems pertaining to the dihydrocoumarin and side-chain moieties involved [12, 13]. Carbon shifts for the coumarin ring systems are given in Table 1; those for side-chain carbons on the relevant formulae.

As anticipated, the shifts for the ring carbons of **1**, **2a** and **2c**, showed four shielded and four deshielded carbons due to the effects of the carbonyl and of the phloroglucinol type substitution. In contrast, **7** and **8** showed only three shielded and three deshielded aromatic carbons because of the reduced C-3–C-4 bond and **6** showed only minor shielding at C-9. Features of



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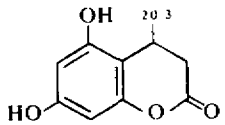

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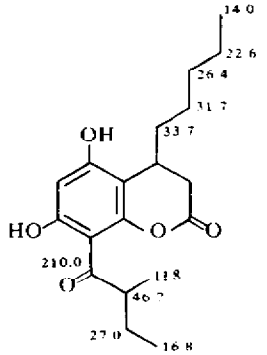

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Table 1. Carbon shifts for coumarin and dihydrocoumarin rings

Carbons	1	2a	2c	6	7	8
2	159.4	159.4	159.4	177.0	168.7	168.0
3	112.7*d*	110.1*d*	110.1*d*	34.5*t*	37.0*t*	34.0*t*
4	154.5*	159.0*	159.0*	24.8*t*	24.9*d*	28.8*d*
5	156.7*	158.8*	158.8*	128.0*d*	153.5*	152.9
6	100.9	102.3	102.3	120.1*d*	99.4*d*	100.0*d*
7	163.2	156.3	156.1	130.4*d*	155.6*	159.0
8	107.3	104.5	104.2	116.5*d*	96.2*d*	104.8
9	159.2	165.4	165.4	153.9	158.1	165,0
10	108.1	109.9	109.9	126.8	107.2	106.8

Signals in any downward column marked with a (*) are interchangeable.

particular note were: (a) the deshielding of the C-2 resonance in dihydrocoumarins relative to coumarins, (b) the reversal of shielding effects from the carbonyl on C-3 and C-4 in dihydrocoumarins (cf. published data for C-15 and C-16 shifts of 17-oxo-steroids [12], (c) the diagnostic deshielding of C-9 in the presence of an 8-buteryl substituent (e.g. **2a**, **2c**, **8**) and (d) the occurrence of the tertiary carbon resonance in **8** at 100 ppm rather than *ca* 110 ppm, thus confirming its presence at C-6 or C-8 and not at C-3.

Of the isoprenyl-type substituents of **1**, **2a** **2c** and **8**, the carbon shifts for the 3,3-dimethylallyl groups were in close agreement with literature data [14]. The 3-methylbuteryl substituents of **1** and **2a** were readily distinguishable from the 2-methylbuteryl isomer found in **2c** and **8** (for shifts see formulae). It proved possible in this work to deduce the structures of isomeric pairs of compounds in a mixture (viz. **2a** and **2c**) and also to determine the presence of relatively small amounts of contaminating coumarins possessing alternative side-chains.

Similarly C-4 substituents were easily resolved. The 4-phenyl moiety of **1** agreed closely with previously published data [11] whilst the alkyl side-chains of **2a**, **2c** and **8** gave carbon shifts showing the reduction in deshielding with increasing distance from the C-2 carbonyl anticipated from previous work [12].

BIOLOGICAL SIGNIFICANCE

The total yield of coumarins obtained from this sample of *M. africana* greatly exceeds that reported previously. This observation agrees with Janzen's suggestion [15] that areas like the Douala-Edea Reserve, where the soil is very impoverished, will prove to be the source of unusually high levels of secondary metabolites. This hypothesis has already been supported by other chemical studies on material from this area [16].

The isolations reported here again confirm the close chemical similarity between *M. africana* and *M. americana* and continue to suggest a close relationship between the two taxa.

EXPERIMENTAL

UV spectra were run in EtOH and IR spectra as KCl discs. PMR spectra were run at 60 MHz in CCl_4, unless otherwise stated, using TMS as internal standard. ^{13}C NMR spectra were run at 25.1 MHz in $CDCl_3$ using FT mode and employing the same internal standard. MS were obtained at 70 eV and elevated temperatures. Mps are uncorr. Petrol refers to the bp 40–60° fraction unless otherwise stated.

Plant material. Bark, seeds and leaves of *Mammea africana* Sabine were collected in the Douala-Edea Forest Reserve, Cameroon, in the summer of 1976. Vouchers, P. G. Waterman and D. McKey 857 and D. McKey and J. S. Gartlan 232 have been deposited at the Herbarium of the Royal Botanic Gardens, Kew.

Isolation of compounds. (a) *From the bark.* Ground bark (355 g) was extracted with petrol, the extract concn and allowed to stand. The crystalline deposit was recrystallized from petrol (bp 60–80°) to give crude **1** (3.9 g). Repeated recrystallization of further oily ppts from hexane gave pure **1** (616 mg). The supernatant of the original concn was subjected to CC over Si gel eluting with petrol containing increasing amounts of EtOAc and gave further **1** followed by **2a** (421 mg). Similar treatment of the $CHCl_3$ of the bark gave further **1**.

(b) *From the leaves.* Ground leaves (237 g) were extracted with petrol. The extract was concn and partitioned with 10% Na_2CO_3 followed by 3% NaOH. Only traces of phenolic compounds could be detected. From the petrol layer a solid separated which on repeated recrystallization gave **3** (223 mg).

(c) *From the seeds.* Ground seeds (155 g) were extracted with petrol, then $CHCl_3$, and finally MeOH. The conc petrol extract was subjected to CC over Si gel eluting with petrol followed by petrol containing slowly increasing amounts of EtOAc to give **4** (66 mg) followed by **1** (30 mg) **2c** (166 mg) and **8** (80 mg). No further compounds could be isolated.

Identification of isolated compounds. Spectroscopic data for compounds **1**, **2a**, **2c** and **4** showed close similarity with those already published [2, 3]. However discrepancies, notably in mps but also in UV and IR maxima, were sufficiently significant to warrant a full description of identification procedures.

Mammea A/AA (6-(3-methylbuteryl)-8-(3,3-dimethylallyl)-5,7-dihydroxy-4-phenylcoumarin; **1**). Yellow needles from hexane, mp 89–100° (Lit. [16A] 98–109°). UV: λ_{max} 241, 285, 341 nm; λ_{max}^{NaOH} 244, 303, 391 sh, 412 nm. IR: ν_{max} 3450 (OH), 1740, 1620 (CO, double band) cm^{-1}. PMR: δ 0.91 (6H, *d*, $CHMe_2$, J = 7 Hz), 1.75, 1.88 (6H,2 × *s*, $=CMe_2$), 2.24 (1H, *m*, $CH_2\underline{C}HMe_2$), 2.88 (2H, *d*, $CHC\underline{H}_2CO$, J = 7 Hz), 3.58 (2H, *d*, $C\underline{H}_2CH$, J = 7 Hz), 5.31 (1H, t, $C\underline{H}CH_2$, J = 7 Hz), 5.96 (1H, *s*, 3-H), 7.53 (5H, *s*, 5 × H-Ar), 9.86 (1H, *s*, replaceable by D_2O, OH), 11.06 (1H, *s*, replaceable by D_2O, OH). MS: Found, M^+ 406.1769; $C_{25}H_{26}O_5$ requires 406.1780; *m/e* 406 (100%), 391 (12), 363 (17), 351 (88), 349 (64), 294 (21), 293 (74), 266 (6), 265 (3). The PMR spectrum of the crude product (mp 83°) showed an additional resonance at δ 1.26. This, together with an ion at *m/e* 372 ($C_{22}H_{28}O_5$) indicated the presence of a small amount of the corresponding 4-*n*-propylcoumarin (**2b**).

Mammea B/BA (6-(3,3-dimethylallyl)-8-(3-methylbuteryl)-5,7-dihydroxy-4-*n*-propylcoumarin; **2a**). Needles from petrol–EtOAc. mp 128° (Lit. [3] 127°). UV: λ_{max} 224, 295, 324 nm. λ_{max}^{NaOH} 222, 255, 333 nm. IR ν_{max} 3345, 2900, 1700, 1600, 1590 cm^{-1}. PMR: δ 1.06 (6H, *d*, $CH\underline{Me}_2$, J = 7 Hz), 1.20 (3H, *t*, $CH_2C\underline{H}_3$, J = 7 Hz), 1.62 (2H, *m*, $CH_2\underline{C}H_2CH_3$), 1.88 (6H, *s*, $=CMe_2$), 2.28 (1H, *m*, $CH_2\underline{C}HMe_2$), 2.96 (2H, *t*, $ArC\underline{H}_2CH_2$, J = 7 Hz), 3.19 (2H, *d*, $COC\underline{H}_2CH$, J = 7 Hz), 3.54 (2H, *d*, $C\underline{H}_2CH$, J = 7 Hz), 5.28 (1H, *t*, $CH_2C\underline{H}$, J = 7 Hz), 6.05 (1H, *s*, 3-H), 7.05 (1H, *s*, replaceable by D_2O, 5-OH), 14.68 (1H, *s*, replaceable by D_2O, 7-OH). MS: Found, M^+ 372.1933; $C_{22}H_{28}O_5$ requires 372.1937; *m/e* 372 (93%), 357 (7), 329 (24), 317 (62), 315 (100), 259 (59), 231 (11), 135 (12).

Friedelan-3-one (**3**). Buff needles from petrol, mp 262° (Lit. [17] 262–263°). $[\alpha]_D$ −19.3 (*c* 1.0, $CHCl_3$), (Lit. [17] −21.0). IR: ν_{max} 2940, 1740, 1460 cm^{-1}. MS: Found, M^+ 426.3872; $C_{30}H_{50}O$ requires 426.3861.

Mammea C/BB (6-(3,3-dimethylallyl)-8-(2-methylbuteryl)-5,7-dihydroxy-4-*n*-pentylcoumarin; **4**). Needles from petrol, mp 81–83° (Lit. [3] 100–101°). UV: λ_{max} 223, 295, 325 nm; λ_{max}^{NaOH} 225, 255, 333 nm. IR ν_{max} 3400, 2960, 1725, 1620, 1400 cm^{-1}. PMR: δ *ca* 1.02 (6H, *t*, 2 × $CH_2C\underline{H}_3$, J = 7 Hz), 1.23 (3H, *d*, $CHC\underline{H}_3$, J = 7 Hz), 1.45 (8H, *m*, 4 × CH_2), 1.82, 1.89 (6H, 2 × *s*, $+CMe_2$), 2.84 (2H, *t*, $Ar{-}C\underline{H}_2CH_2$, J = 7.5 Hz), 3.49

(2H, *d*, $CHC\underline{H}_2$, J = 7 Hz), 3.84 (1H, *m*, $COC\underline{H}(Me)CH_2$), 5.26 (1H, *t*, $C\underline{H}CH_2$, J = 7 Hz), 5.91 (1H, *s*, 3-H), 7.09 (1H, *s*, replaceable by D_2O, 5-OH), 14.65 (1H, *s*, replaceable by D_2O, 7-OH). MS: Found, M^+ 400.2246; $C_{24}H_{32}O_5$ requires 400.2250; *m/e* 400 (48%), 345 (19), 343 (100), 329 (11), 287 (38), 259 (34), 135 (2).

Mammea B/BB (6-(3,3-dimethylallyl)-8-(2-methylbuteryl)-5,7-dihydroxy-4-*n*-propylcoumarin; **2c**). Pale yellow needles from petrol, mp 72–74° (Lit. [3] 122°). UV: λ_{max} 223, 292, 334 sh. nm; λ_{max}^{NaOH} 223, 245 sh, 317, 333 nm. IR: ν_{max} 3300, 2995, 1730, 1625, 1600, 1430 cm^{-1}. PMR: δ 1.01 (6H, *t*, 2 × $CH_2C\underline{H}_3$, J = 7 Hz), 1.18 (3H, *d*, $CHC\underline{H}_3$, J = 7 Hz), 1.48–1.66 (4H, *m*, 2 × $3H_2$), 1.80, 1.87 (6H, 2 × *s*, $=CMe_2$), 2.98 (2H, *t*, $Ar-C\underline{H}_2CH_2$, J = 7 Hz), 3.55 (2H, *d*, $CHC\underline{H}_2$, J = 7 Hz), 3.86 (1H, *m*, $COC\underline{H}(Me)CH_2$), 5.22 (1H, *t*, $C\underline{H}CH_2$, J = 7 Hz), 5.88 (1H, *s*, 3-H), 7.52 (1H, *s*, replaceable by D_2O, 5-OH), 14.65 (1H, *s*, replaceable by D_2O, 7-OH). MS: Found, M^+ 372.1936; $C_{22}H_{28}O_5$ requires 372.1937; *m/e* 372 (62%), 329 (9), 317 (32), 315 (100), 259 (46), 231 (8), 135 (9). The occurrence in the PMR spectrum of a signal at δ 3.26 and of a fragment at *m/e* 317 in the MS suggested the material was contaminated with **2a**. This was confirmed by a ^{13}C NMR study which showed small resonances attributable to the 3-methylbuteryl side-chain of **2a**.

Dihydromammea C/OB (8-(2-methylbuteryl)-5,7-dihydroxy-4-*n*-pentyl-3,4-dihydrocoumarin; **8**). Needles from petrol, mp 125°. $[\alpha]_D^{24}$ +127° (*c* 0.25, $CHCl_3$). UV: λ_{max} 233, 286, 325 nm (log ε 4.21, 4.23, 3.88); λ_{max}^{NaOH} 212, 332 nm. IR: ν_{max} 3500, 2995, 1780, 1650, 1620, 1505, 1440 cm^{-1}. PMR: δ 0.96 (6H, *t*, 2 × $CH_2C\underline{H}_3$, J = 7 Hz), 1.17 (3H, *d*, $CHC\underline{H}_3$, J = 7 Hz), 1.30–1.70 (10H, *m*, 5 × CH_2), 2.85 (2H, ABX, $CHC\underline{H}_2COO$), 3.34 (1H, *m*, $CH_2C\underline{H}C_5H_{11}$), 3.73 (1H, *m*, $COC\underline{H}(Me)CH_2$) 6.32 (1H, *s*, 6-H), 7.45 (1H, *s*, replaceable by D_2O, 5-OH), 13.69 (1H, *s*, replaceable by D_2O, 7-OH). MS: Found, M^+ 334.1781; $C_{19}H_{26}O_5$ requires 334.1780; *m/e* 334 (16%), 278 (21), 277 (100), 263 (12), 235 (19), 165 (37).

Dihydrocoumarin (**6**). UV: λ_{max} 222, 275, 280 nm. IR: ν_{max} 1765, 1610, 1440 cm^{-1}. PMR: ($CDCl_3$, TMS) 2.75–2.95 (4H, *m*, CH_2CH_2), 6.75–7.30 (4H, *m*, 4 × H-Ar).

Synthesis of 5,7-dihydroxy-4-methyldihydrocoumarin (**7**). 5,7-Dihydroxy-4-methylcoumarin (4 g) was dissolved in 10% NaOH (120 ml) and Ni/Al alloy (10 g) added. The reaction mixture was heated to 90° for 1 hr, filtered, and acidified with conc HCl to give a ppt. The mixture was extracted into EtOAc and purified by PLC on Si gel, eluting with Et_2O, to give **7** (200 mg) as needles, mp 108°. UV: λ_{max} 229, 278, 283 nm; λ_{max}^{NaOH} 284, 299 nm. IR: ν_{max} 3225, 1760, 1640, 1560 cm^{-1}. PMR: (Me_2CO-d_6, TMS) δ 1.13 (3H, *d*, $CHC\underline{H}_3$, J = 7 Hz), 2.40–3.10 (2H, ABX, $CHC\underline{H}_2COO$), 3.20–3.70 (1H, *m*, $CH_3C\underline{H}CH_2$), 6.10, 6.30 (2H, ABq, 6-H, 8-H, J = 2 Hz). MS: Found, M^+ 194.0570; $C_{10}H_{10}O_4$ requires 194.0579; *m/e* 194 (67), 180 (15), 179 (100), 152 (36), 151 (9), 137 (4).

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