Efficient *ortho*-Oxidation of Phenols with Diacyl Peroxides

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A stable symmetric diacyl peroxide, *m*-chlorobenzoyl peroxide (*m*CBPO), and an asymmetric diacyl peroxide, chloroacetyl *m*-chlorobenzoyl peroxide (CAMCBPO), were synthesized from *m*-chloroperbenzoic acid. Both peroxides oxidized phenols selectively at the *ortho* position predoninantly. CAMCBPO gave *para*-oxidized compounds as minor products from some phenols. The improvement of the yield of *ortho*-oxidation of phenols with *m*CBPO was also reported.

Key words *ortho*-oxidation; phenol; stable diacyl peroxide; *m*-chlorobenzoyl peroxide; chloroacetyl *m*-chlorobenzoyl peroxide; chloroacetic acid

There are many natural catechols which show various biological activities, *e.g.*, anti-oxidant,[1] anti-methicillin-resistant *Staphylococcus aureus* (MRSA) and vancomycin-resistant *Enterococcus* (VRE),[2] anti-tubercular,[3] anti-bacterial,[4—9] anti-plasmodial,[10] anti-viral,[11,12] anti-tumor,[13—15] and anti-platelet[16] activities. Natural catechol derivatives are easily oxidized by oxygen or chemical reagents. Benzeneseleninic anhydride,[17] 2-iodoxybenzoic acid (IBX)[18,19] and iodobenzene diacetate[20,21] are well known reagents for *ortho*-oxidation of phenol to give *ortho*-quinone or *ortho*-hydroxy-*para*-quinone methide, although sometimes a complex mixture is formed. Dibenzoyl peroxide is commonly used as an initiator of polymer synthesis and an effective reagent for *ortho*-oxidation of phenols to give catechol monoesters. However, dibenzoyl peroxide is unstable and has caused large explosions in industrial plants, *e.g.*, at Itabashi in Japan (1990) and in northern Taiwan (2001).[22] In the previous synthesis of abietaquinone methide[3] (**1**) with anti-MRSA and anti-VRE activities, we reported *ortho*-oxidation of phenols using a stable diacyl peroxide, *m*-chlorobenzoyl peroxide (*m*CBPO, **2**) which was synthesized from *meta*-chloroperbenzoic acid.[23] The *ortho*-oxidation of a diterpene phenol with *m*CBPO gave the corresponding catechol ester in moderate yield, but the oxidation of other small phenols gave lower yields. We thus planned to improve the *ortho*-oxidation of phenols with diacyl peroxides, a stable and nontoxic reagent. We report herein a novel *ortho*-oxidation reaction of phenol using the asymmetric diacyl peroxide which was synthesized from *m*-chloroperbenzoic acid, together with the improvement of the yield of *ortho*-oxidation of phenols with the symmetric diacyl peroxide, *m*CBPO.

***ortho*-Oxidation of Phenols with the Symmetric Diacyl Peroxide, *m*CBPO** Previously, we synthesized abietaquinone methide **1**, *via* the *ortho*-oxidation of ferruginol (**3**) with *m*CBPO at ambient temperature (Fig. 1).[23] Some small phenols, *e.g. o*-cresol, *m*-cresol, *p*-cresol, 2,4-xylenol and 3,5-xylenol, however, were not oxidized with *m*CBPO at ambient temperature. Kubota and Takeuchi reported the unexpected formation of *m*CBPO **2** by the heating of *m*CPBA in dimethyl formamide (DMF) which was accompanied by an explosion.[24] The formation of *m*CBPO after the explosion indicates that *m*CBPO is stable under high temperatures. In fact, solid *m*CBPO melts at over 110 °C and exhibits slow foaming when heated in a glass tube. They also foresaw that severe explosion of *m*CBPO in DMF over 125 °C from the differential thermal analysis, and improvement of the reaction condition using CH_2Cl_2 solution to avoid the incident. Thus we tried the reaction of phenols with *m*CBPO at refluxing temperature of CH_2Cl_2 and $CHCl_3$. Phenols were safely oxidized with *m*CBPO even at refluxing temperature in chloroform. The reaction mixtures were reduced with $LiAlH_4$ (LAH) and then acetylated with acetic anhydride and pyridine. The mixture was chromatographed on silica gel to give catechol diacetates that was analyzed by NMR spectroscopy without further purification. The reaction yields were estimated by measuring the ^{1}H-NMR spectra of these catechol diacetates (Table 1, Fig. 2). The phenols were oxidized at the *ortho*-position selectively. As mentioned above, small phenols *e.g. o*-cresol, *m*-cresol, *p*-cresol, 2,4-xylenol and 3,5-xylenol, could not be oxidized by the previous experimental condition at ambient temperature.[23] Many phenols, however, were oxidized at refluxing temperature to show the reaction condition at refluxing temperature is superior to that at ambient temperature. Ferruginol which has three alkyl substitutents on the phenol ring was oxidized at ambient temperature in 50% yield.[23] *ortho*-Substituted phenols, however, were oxidized by this reaction (Table 1: entries 5, 8, 11) in less yield. Asymmetric diacyl peroxides were then prepared and used *in situ* for the oxidation of phenols.

***ortho*-Oxidation of Phenols Using Asymmetric Diacyl Peroxides** Various carboxylic acids were treated with *meta*-chloroperbenzoic acid (*m*CPBA: content >68%, product of Tokyo Kasei) and dicyclohexylcarbodiimide (DCC) (Table 2). Asymmetric diacyl peroxides were presumed to be

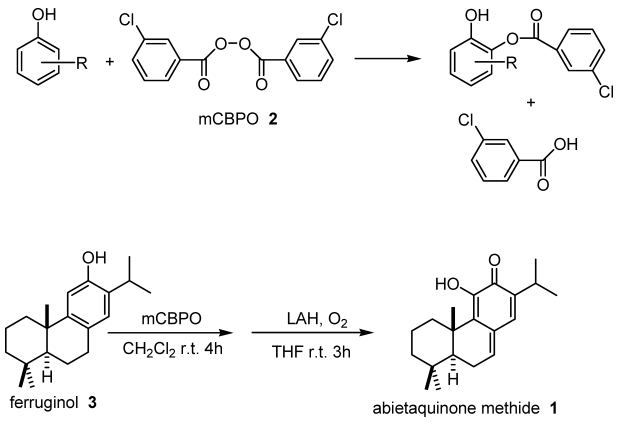

Fig. 1. *ortho*-Oxidation of Phenols with *m*CBPO

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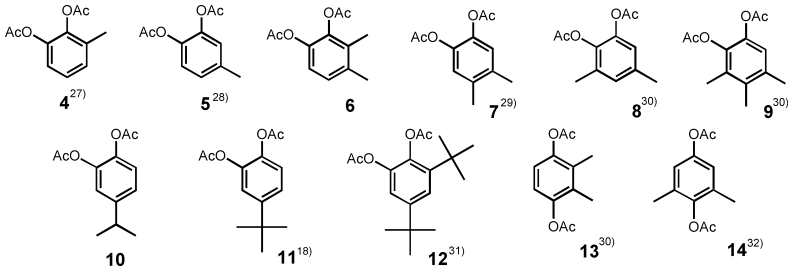


Fig. 2. Oxidation Products of Various Phenols with *m*CBPO and Chloroacetyl *m*-Chlorobenzoyl Peroxide (CAMCBPO)

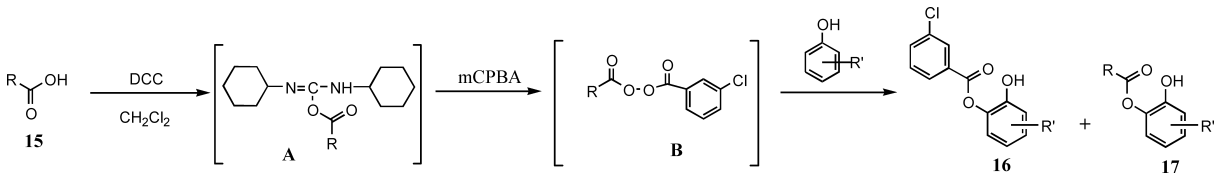


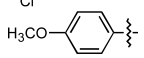
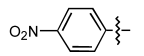
Fig. 3. Synthesis of Asymmetric Diacyl Peroxides and Oxidation of Phenols with Asymmetric Diacyl Peroxides

Table 1. Oxidation of Phenols with *m*CBPO and with CAMCBPO

Entry	Phenol	*m*CBPO		CAMCBPO	
		Products	Yield (%)[a)]	Products	Yield (%)[a)]
1	*o*-Cresol	**4**	n.r.	**4**	Trace
2	*m*-Cresol	**5**	35	**5**	Trace
3	*p*-Cresol	**5**	75	**5**	25
4	2,3-Xylenol	**6**	11	**6**+**13**	27 (2 : 1)
5	3,4-Xylenol	**6**+**7**	39 (1 : 3)	**6**+**7**	26 (1 : 6)
6	3,5-Xylenol	**8**	32	**8**+**14**	45 (2 : 1)
7	2,4-Xylenol		n.r.	**8**	18
8	3,4,5-Trimethylphenol	**9**	56	**9**	25
9	4-Isopropylphenol	**10**	29	**10**	32
10	4-*tert*-Butylphenol	**11**	17	**11**	53
11	2,4-di-*tert*-Butylphenol		n.r.	**12**	51

CAMCBPO: chloroacetyl *m*-chlorobenzoyl peroxide. *a*) Estimated by ^{1}H-NMR of the diacetate. n.r.: no reaction.

Table 2. Oxidation of 3-Methoxyphenol with Asymmetric Diacyl Peroxides

Entry	R group of RCOOH	pK_a[25,26)]	Yield (%)
1	CH_3-	4.76	Trace
2	CH_2I-	2.90	17[a)]
3	CH_2Br-	2.82	29[a)]
4	CH_2Cl-	2.66	53[a)]
5	$CHCl_2$-	1.30	n.r.
6	CCl_3-	0.46	n.r.
7		4.19	n.r.
8		3.83	Trace
9		3.47	Trace
10		3.43	Trace

a) Estimated by ^{1}H-NMR of the diacetate. n.r.: no reaction

formed as the intermediate (**B**) by condensation with the corresponding acids (Fig. 3). The oxidation of 3-methoxyphenol was examined *in situ* using the synthesized asymmetric diacyl peroxides. The reaction mixtures were reduced with $LiAlH_4$ and then acetylated with acetic anhydride and pyridine. The reaction yields were estimated by measuring the ^{1}H-NMR spectra of the catechol diacetate (4-methoxyphenylene-1,2-diacetate[18)]) produced. Chloroacetic acid (pK_a 2.66)[25,26)] gave a moderate yield. The formation of chloroacetyl *meta*-chlorobenzoyl peroxide (CAMCBPO) was presumed from the ^{1}H-NMR spectrum of the reaction mixture of chloroacetic acid, DCC and *m*CPBA in $CDCl_3$. The ^{1}H-NMR ($CDCl_3$, 600 MHz) of the reaction mixture showed the signals due to CAMCBPO [δ: 8.07 (1H, br s), 7.98 (1H, br d, J=8.1 Hz), 7.59 (1H, br d, J=8.1 Hz), 7.42 (1H, t, J=8.1 Hz) , 4.13 (2H, s)] and *meta*-chlorobenzoic anhydride [δ: 8.11 (0.6H, t, J=1.8, 1.8 Hz), 8.04 (0.8H, br d, J=8.1 Hz), 7.67 (0.8H, br d, J=8.1 Hz), 7.50 (0.8H, t, J=8.1 Hz)], whereas the signals due to chloroacetic *meta*-chlorobenzoic anhydride were not observed under this reaction condition.

The reaction conditions were optimized by adjusting reagent quantities (chloroacetic acid, *m*CPBA and DCC), temperature and reaction times for the oxidation of 4-*tert*-butylphenol. A moderate yield was obtained under the reaction conditions using 2.0 eq of chloroacetic acid, 2.2 eq of DCC and 2.8 eq of *m*CPBA, at 0 °C to room temperature for 66 h. The oxidation of various phenols was subsequently examined using these conditions (Tables 1, 3).

The yields and products with these reaction conditions were different from those by *m*CBPO. *m*CBPO could be formed in Table 2 entry 8, but the yield was lower than previous result by this reaction condition. Bicyclic phenols and phenols with bulky alkyl groups gave increased yields. The majority of phenols were oxidized predominantly at the *ortho* position, but some were oxidized at both the *ortho* and *para* positions (Table 1: entries 4, 6; Table 3: entry 1). We previously proposed the mechanism of the oxidation with *m*CBPO through a [3,3] sigmatropic rearrangement of the peroxyacid ester of phenol to give the catechol ester selectively.[23)] These results, however, suggested that the reaction mechanism of the oxidation with asymmetric the diacyl peroxide (CAMCBPO) is different. The products suggested the formation of

a radical intermediate that can oxidize at either the *ortho* or *para* positions (Fig. 4). It is expected that CAMCBPO is more reactive than *m*CBPO towards decomposition into radical intermediates. However, the oxidation of 4-*tert*-butylanisole was attempted unsuccessfully with these reaction conditions, with no oxidation product observed. While the reaction mechanism of the *ortho*-oxidation of phenols with symmetric or asymmetric diacyl peroxides are still unknown, the utility of this reaction to prepare catechols from phenols is clear.

Conclusion

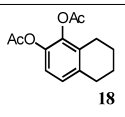
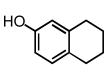
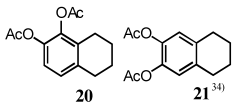
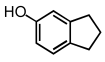
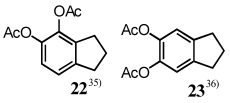
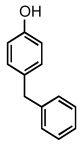
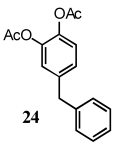
The *ortho*-oxidation of phenols with the stable diacyl peroxide, *m*CBPO was improved. An asymmetric diacyl peroxide, CAMCBPO was prepared and oxidized phenols *in situ* safely. These results warrant further investigation of these reagents for organic reactions and polymer syntheses.

Experimental

General Procedures NMR spectra were measured on a JEOL Alpha-600 (^{1}H: 600 MHz, ^{13}C: 150.8 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard (*J*-values in Hz). IR spectra were measured on a JEOL JIR-WINSPEC 50 infrared spectrometer. Mass spectra were recorded on a JEOL JMS-K9 UltraQuad GC/MS spectrometer. Melting points (mp) were measured on a MEL-TEMP (Laboratory Device) and were uncorrected. TLC was carried out on silica gel 60 (0.25-mm thickness) with fluorescent indicator (Macherey-Nagel). Silica gel (6 nm, BW-127ZH, Fuji Silysia Chemical Ltd.) was used for column chromatography.

***ortho*-Oxidation of Phenols with *m*CBPO under Reflux** To a solution of substituted phenol (0.25 mmol) in $CHCl_3$ (3 ml), was added *m*CBPO (0.3 mmol) and the solution was heated under reflux for 16 h under argon.

Table 3. Oxidation of Phenols with CAMCBPO

Entry	Phenol	Product	Yield (%)[a)]
1		 **18** **19**[33)]	31 (5 : 1)
2		 **20** **21**[34)]	67 (1 : 2)
3		 **22**[35)] **23**[36)]	29 (1 : 3)
4		 **24**	27

a) Estimated by ^{1}H-NMR of the diacetate.

The reaction mixture was evaporated. The residue was dissolved in tetrahydrofuran (THF) (3 ml) and LAH (228 mg, 6 mmol) was added. After stirring at 0 °C for 1 h, the reaction was stopped with methanol and EtOAc. The organic layer was successively washed with 1 M HCl, saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and evaporated. The residue was dissolved in pyridine (2 ml) and Ac_2O (1 ml) and the solution was stirred at ambient temperature for 1—2 h. The progress of the reaction was followed by thin layer chromatography. The reaction was quenched with methanol and the organic layer was successively washed with 1 M HCl, saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and evaporated. The reaction mixture was chromatographed on a silica gel column with EtOAc–hexane to give diacetates. The yields were estimated by comparing the integration of the signals in the ^{1}H-NMR spectra of the diacetates to that of the additive standard, dioxane.

Oxidation of Phenol with Chloroacetic Acid, *meta*-Chloroperbenzoic Acid and Dicyclohexylcarbodiimide A solution of chloroacetic acid (283 mg, 3.0 mmol) and DCC (680 mg, 3.3 mmol) in CH_2Cl_2 (15 ml) was stirred for 15 min and *m*CPBA (725 mg, less than 4.2 mmol: content >68%: Tokyo Kasei) was added. The solution was stirred for an additional 30 min and phenol (1.5 mmol) was added. After stirring at 0 °C to room temperature for 66 h, the reaction mixture was filtered to remove solids of dicyclohexylurea. The filtrate was evaporated and the residue was dissolved in EtOAc. The EtOAc solution was successively washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and evaporated. The residue was dissolved in THF (3 ml) and LAH (228 mg, 6 mmol) was added. After stirring at 0 °C for 1 h, the reaction was stopped with methanol and EtOAc. The organic layer was successively washed with 1 M HCl, saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and evaporated. The residue was dissolved in pyridine (2 ml) and Ac_2O (1 ml) and the solution was stirred at ambient temperature for 1—2 h. The progress of the reaction was followed by thin layer chromatography. The reaction was quenched with methanol and the organic layer was successively washed with 1 M HCl, saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and evaporated. The reaction mixture was chromatographed on a silica gel column with EtOAc–hexane to give diacetate. The yields were estimated by comparing the integration of the signals in the ^{1}H-NMR spectra of the diacetates to that of the additive standard, dioxane.

3,4-Dimethylphenylene-1,2-diacetate (**6**) and 2,3-Dimethylphenylene-1,4-diacetae (**13**): Yellow oil; ^{1}H-NMR ($CDCl_3$, 600 MHz) δ: 7.05 (1H, d, J=8.4 Hz), 6.92 (1H, d, J=8.4 Hz), 6.88 (0.5H, s), 2.32 (4.5H, s), 2.27 (6H, s), 2.09 (1.5H, s), 2.08 (3H, s); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ: 169.34, 168.69, 168.26, 146.77, 140.63, 140.29, 135.75, 130.37, 127.43, 119.84, 20.81, 20.63, 20.33, 19.80, 13.02, 12.82; IR cm^{-1} (KBr) 2929, 2856, 1762, 1650, 1461, 1367, 1211, 1178, 1078, 1027; LR-EI-MS *m/z* (relative intensity %) 222 (M^+, 8), 180 (25), 138 (100), 123 (13), 107 (5), 91 (11), 79 (15), 65 (13); HR-ESI-MS *m/z*: 245.0840 (Calcd for $C_{12}H_{14}O_4Na(M+Na)^+$ 245.0790).

4,5-Dimethylphenylene-1,2-diacetate (**7**) and 3,4-Dimethylphenylene-1,2-diacetate (**6**): Yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.04 (0.3H, d, J=8.3 Hz), 6.93 (2H, s), 6.91 (0.3H, d, J=8.3 Hz), 2.32 (1H, s), 2.27 (8H, s), 2.22 (6H, s), 2.08 (1H, s); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 168.43, 168.04, 140.50, 140.17, 139.36, 135.58, 135.10, 130.41, 127.28, 123.94, 119.72, 20.59, 20.32, 19.79, 19.36; IR cm^{-1} (KBr) 2971, 2933, 2850, 1766, 1633, 1504, 1371, 1214. 1178, 1081; LR-EI-MS *m/z* (relative intensity %) 222 (M^+, 8), 180 (38), 138 (100), 123 (20), 109 (5), 91 (18), 79 (22), 65 (19)); HR-ESI-MS *m/z*: 245.0833 (Calcd for $C_{12}H_{14}O_4Na(M+Na)^+$ 245.0790).

4-Isopropylphenylene-1,2-diacetate (**10**): Yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.10 (1H, dd, J=8.1, 2.0 Hz), 7.01 (1H, d, J=8.1 Hz), 2.40 (1H, sept, J=6.8 Hz), 2.29 (3H, s), 2.28 (3H, s), 1,24 (6H, d, J=6.8 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 168.21, 168.07, 147.41, 141.56, 139.64, 124.37, 122.79, 121.05, 33.50, 23.76, 20.56, 20.54; IR cm^{-1} (NaCl) 2950,

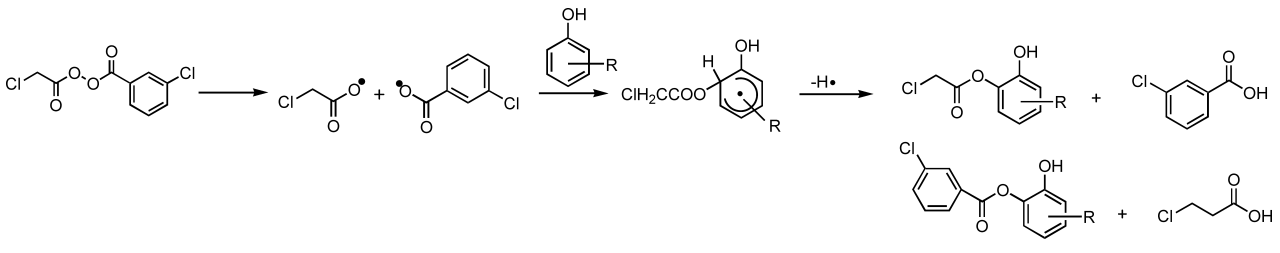


Fig. 4. Presumed Reaction Mechanism of Oxidation of Phenols with CAMCBPO

2930, 2872, 1770, 1597, 1502, 1423, 1263, 1217, 1190, 1169, 1117, 1045, 1016, 953, 899, 876, 849, 831, 798, 598, 553, 525; LR-EI-MS *m/z* (relative intensity %) 236 (M^+, 7), 152 (99), 137 (100), 107 (8), 91 (37), 79 (38), 43 (100); HR-ESI-MS *m/z*: 237.1125 (Calcd for $C_{13}H_{17}O_4(M+H)^+$ 237.1127).

5,6,7,8-Tetrahydronaphthalene-1,2-diacetate (**18**) and 5,6,7,8-Tetrahydronaphthalene-1,4-diacetate (**19**): Yellow powder; ^{1}H-NMR ($CDCl_3$, 600 MHz) δ: 6.98 (1H, d, J=8.4 Hz), 6.92 (1H, d, J=8.4 Hz), 6.86 (2H, s), 2.76—2.73 (8H, m), 2.30 (3H, s), 2.27—2.26 (6H, m), 1.77—1.76 (8H, m); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ: 168.50, 168.46, 167.93, 140.12, 139.28, 136.21, 135.53, 130.98, 126.82, 123.13, 119.74, 28.88, 28.75, 23.27, 22.54, 21.88, 20.43, 20.40, 20.08; IR cm^{-1} (KBr) 3026, 2950, 2935, 2908, 2860, 2841, 1765, 1498, 1433, 1371, 1207, 1178, 1086, 1063, 920, 881, 864, 802, 652, 594, 559; HR-ESI-MS *m/z*: 249.1147 (Calcd for $C_{14}H_{17}O_4(M+H)^+$ 249.1127).

4-Benzylphenylene-1,2-diacetate (**24**): Yellow oil; ^{1}H-NMR ($CDCl_3$, 600 MHz) δ: 7.30 (2H, t, J=7.3 Hz), 7.22 (1H, t, J=7.3 Hz), 7.18 (2H, d, J=7.3 Hz), 7.09 (1H, d, J=8.1 Hz), 7.05 (1H, dd, J=8.1, 1.8 Hz), 6.97 (1H, d, J=1.8 Hz), 3.97 (2H, s), 2.27 (3H, s), 2.26 (3H, s); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ: 168.26, 168.15, 141.81, 140.20, 139.90, 128.48, 126.82, 126.26, 123.54, 123.08, 41.04, 20.50, 20.48; IR cm^{-1} (NaCl) 3086, 3064, 3028, 2931, 2854, 1768, 1597, 1508, 1454, 1425, 1365, 1258, 1217, 1108, 1012, 964, 904, 841, 733, 698, 592; EI-MS *m/z* (relative intensity %): 284 (M^+, 1), 242 (23), 200 (80), 122 (29), 91 (17), 77 (10), 43 (100); HR-ESI-MS *m/z*: 307.0930 (Calcd for $C_{17}H_{16}O_4Na(M+Na)^+$).

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