Supplementary Material for Organic & Biomolecular Chemistry

Syntheses in enantiopure form of four diastereoisomeric naphthopyranquinones derived from aphid insect pigments

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Experimental

Ethyl (α′*S* and *R*, 2*S*)-2-(2′-benzyloxy-3′-bromo-5′-*t*-butyldimethylsilyloxy-α′-methylbenzyloxy)propanoate 29

Using the method described above for the synthesis of the benzyl-epimeric mixture of methyl esters **22**, but with ethyl (*S*)-lactate replacing methyl (*R*)-lactate, the benzyl-epimeric mixture of ethyl esters **29** was assembled in a yield of 92%. (Found: C, 58.55; H, 6.8; M^+, 538.1588 and 536.1604. $C_{26}H_{37}BrO_5Si$ requires C, 58.1; H, 6.9; M(^{81}Br), 538.1573 and M(^{79}Br), 536.1594); δ_H (600 MHz, mixture of two diastereoisomers) 0.198 and 0.204 (each 3H, s, OSi(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.21 (6H, s, OSi(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.98 and 0.99 (each 9H, s, OSi(CH$_3$)$_2$C(C*H*$_3$)$_3$), 1.34 and 1.35 (each 3H, d, *J* 6.9 Hz, 2-CH$_3$), 1.36 and 1.41 (each 3H, d, *J* 6.4 Hz, α′-CH$_3$), 3.78 and 3.87 (each 1H, q, *J* 6.8 Hz, 2-H), 4.01-4.17 (4H, m, C*H*$_2$CH$_3$), 4.81 and 4.93 (2H, AB quartet, *J* 10.7 Hz, OCH$_2$Ph), 4.85 and

4.86 (each 1H, q, 6.4 Hz, α′-H), 4.94 and 4.97 (2H, AB quartet, *J* 11.0 Hz, OCH_2Ph), 6.88 and 7.01 (each 1H, d, *J* 2.9 Hz, 4′ and 6′-H), 6.93 and 6.99 (each 1H, d, *J* 2.9 Hz, 4′ and 6′-H) and 7.33-7.51 (10H, m, 2 x C_6H_5); δ_C (150 MHz, mixture of two diastereoisomers) –4.58 and –4.56 ($OSi(CH_3)_2C(CH_3)_3$), -4.51 (2 x $OSi(CH_3)_2C(CH_3)_3$), 14.06 and 14.11 (CH_2CH_3), 18.1 and 19.0 (C-3), 18.2 ($OSi(CH_3)_2C(CH_3)_3$), 23.2 and 23.6 (α′-CH_3), 25.6 ($OSi(CH_3)_2C(CH_3)_3$), 60.7 and 60.8 (CH_2CH_3), 70.9 and 71.4 (C-α′), 72.3 and 72.6 (C-2), 75.51 and 75.55 (OCH_2Ph), 116.9 and 117.2 (C-3′), 117.1 and 117.8 (C-6′),[a] 123.8 and 124.1 (C-4′),[a] 127.99 and 128.01 (C-2″ and C-6″), 128.20 and 128.22 (C-4″), 128.48 and 128.52 (C-3″ and C-5″), 136.7 and 136.9 (C-1′),[c] 138.9 and 139.1 (C-1″),[c] 147.0 and 147.5 (C-2′),[d] 1152.7 and 152.9 (C-5′),[d] 172.7 and 173.5 (C=O); m/z 538 [M^+ (^{81}Br), 5%], 536 [M^+ (^{79}Br), 5%], 447 (40), 445 (38), 421 (10), 419 (10), 347 (37), 345 (35), 331 (18), 330 (38), 329 (41), 328 (37), 327 (23), and 91 (100).

(α′*R*, 2*S*)-2-(2′-Benzyloxy-3′-bromo-5′-*t*-butyldimethylsilyloxy-α′-methyl-benzyloxy)propanol 26 and (α′*S*, 2*R*)-2-(2′-benzyloxy-3′-bromo-5′-*t*-butyldimethylsilyloxy-α′-methylbenzyloxy)propanol 31

Using the method described above for the reduction of the mixture of methyl lactates **22** to form the alcohols **23** and **30**, the mixture of ethyl lactates **29** was reduced with a limited amount of lithium aluminium hydride to provide the chromatographically separable alcohols **26** and **31**, for which the specific rotations were +58.8 ° and –22.9 ° (*c* 1.0 in $CHCl_3$), in good agreement, but for sign, with those of the enantiomers **30** and **23** respectively.

(α′*S*, 2*R*)-2-(2′-Benzyloxy-3′-bromo-5′-*t*-butyldimethylsilyloxy-α′-methylbenzyloxy)-propanal 27

According to the method described above for the preparation of the aldehyde **24** from the alcohol **23**, the (α′*R*, 2*S*) alcohol **26** (200 mg, 0.4 mmol) was converted, after chromatography (radial, 5% ethyl acetate-hexane), into the aldehyde **27** as a colourless oil (169 mg, 85%) $[\alpha]_D$ +21.3 ° (*c* 1.0 in $CHCl_3$); (Found: C, 59.2; H, 6.95; M^+, 492.1337. $C_{24}H_{33}BrO_4Si$ requires C, 58.5; H, 6.75; M(^{79}Br), 492.1331); υ_{max}(film)/cm^{-1} 1739 (C=O) and 1596 and 1495 (C=C); δ_H 0.20 (6H, s, OSi(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.98 (9H, s, OSi(CH$_3$)$_2$C(C*H*$_3$)$_3$), 1.21 (3H, d, *J* 6.8 Hz, 2-CH$_3$), 1.37 (3H, d, *J* 6.4 Hz, α′-CH$_3$), 3.61 (1H. dq, *J* 1.2 and 6.8 Hz, 2-H), 4.87 (1H, q, *J* 6.4 Hz, α′-H), 4.94 (2H, s, OCH$_2$), 6.90 (1H, d, *J* 2.9 Hz, 6′-H), 7.02 (1H, d, *J* 2.9 Hz, 4′-H) and 7.34-7.49 (5H, m, C$_6$H$_5$), 9.49 (1H, d, *J* 1.2 Hz, CHO); δ_C -4.5, (OSi(*C*H$_3$)$_2$C(CH$_3$)$_3$), 15.0 (C-3), 18.2 (OSi(CH$_3$)$_2$*C*(CH$_3$)$_3$, 23.4 (α′-CH$_3$), 25.6 (OSi(CH$_3$)$_2$C(*C*H$_3$)$_3$), 70.6 (C-2), 75.8 (OCH$_2$), 78.1 (C-α′), 117.2 (C-3′), 117.4 (C-6′), 124.4 (C-4′), 128.1 (C-2″ and C-6″), 128.3 (C-4″), 128.6 (C-3″ and C-5″), 136.6 (C-1″), 138.7 (C-1′), 147.3 (C-2′), 152.9 (C-5′) and 202.6 (C-1); m/z 494 [M^+ (^{81}Br), 1%], 492 [M^+ (^{79}Br), 1%], 359 (19), 357 (20), 329 (32), 191 (45), 91 (86) and 73 (100).

(α′*R*, 2*S*)-2-(2′-Benzyloxy-3′-bromo-5′-hydroxy-α′-methylbenzyloxy)propanal 28

According to the method described above for the preparation of the phenolic aldehyde **25** from the (α′*R*, 2*R*) aldehyde **24**, the (α′*R*, 2*S*) aldehyde **27** (130 mg, 0.26 mmol) was converted, after chromatography (radial, 5% ethyl acetate-hexane), into the phenolic

aldehyde **28** as a colourless oil (115 mg, 76%); (Found: $(M\text{-}H_2O)^+$, 360.0352. $C_{18}H_{17}BrO_3$ requires M(^{79}Br), 360.0361); υ_{max}(film)/cm^{-1} 3386 (OH), 1732 (C=O) and 1602, 1575 and 1498 (C=C); δ_H 1.23 (3H, d, *J* 6.9 Hz, 2-CH_3), 1.36 (3H, d, *J* 6.4 Hz, α′-CH_3), 3.68 (1H, dq, *J* 0.9 and 6.9 Hz, 2-H), 4.87 (1H, q, *J* 6.4 Hz, α′-H), 4.90 and 4.95 (each 1H, d, *J* 11.1 Hz, OCH_2), 4.85-4.97 (1H, br. s, OH), 6.96 (1H, d, *J* 2.9 Hz, 6′-H), 7.04 (1H, d, *J* 2.9 Hz, 4′-H), 7.35-7.49 (5H, m, C_6H_5) and 9.45 (1H, d, *J* 0.9 Hz, CHO); δ_C 14.9 (C-3), 23.3 (α′-CH_3), 70.8 (C-2), 75.9 (OCH_2), 78.1 (C-α′), 112.8 (C-6′), 117.6 (C-3′), 120.0 (C-4′), 128.2 (C-2″ and C-6″), 128.4 (C-4″), 128.6 (C-3″ and C-5″), 136.6 (C-1″), 138.7 (C-1′), 146.4 (C-2′), 153.4 (C-5′) and 202.8 (C-1); m/z 362 [$(M\text{-}H_2O)^+$ (^{81}Br), 4%], 360 [$(M\text{-}H_2O)^+$ (^{79}Br), 4%], 167 (6), 149 (22) and 91 (100).

(1*R*,3*R*,4*R*)-7-Bromo-3,4-dihydro-4-hydroxy-1,3-dimethylbenzo[*c*]pyran-5,8-quinone 59 and (1*R*,3*R*,4*R*)-3,4-dihydro-4-hydroxy-1,3-dimethylbenzo[*c*]pyran-5-8-quinone 60

A solution of compound **36** (168 mg, 0.43 mmol) in dry ethyl acetate (15 cm^3) was stirred with 10% palladium on carbon catalyst (100 mg,) under a hydrogen atmosphere for 1.5 h. The mixture was filtered through celite, concentrated and purified through rapid chromatography (radial, 35% ethyl acetate-hexane) to afford a oily unstable mixture **37** and **38** (130 mg, 0.43 mmol). This was immediately dissolved in acetonitrile (15 cm^3) and cerium(IV) ammonium nitrate (470 mg, 0.86 mmol) in water (3 cm^3) was added drop-wise to the solution. After 20 min the reaction was quenched with water and exhaustively extracted with dichloromethane. The residue obtained upon work-up was chromatographed (radial, 15-25% ethyl acetate-hexane) to give both the brominated

quinone **59** and the debrominated quinone **60** as bright yellow crystals. The product of higher R_F was identified as **59** (63 mg, 51%) m.p. 144-145 °C (dichloromethane-hexane) $[\alpha]_D$ +94 ° (*c* in 1.0 $CHCl_3$); (Found: C, 46.25; H, 4.0; $(M\text{-}H_2O)^+$, 267.9723. $C_{11}H_{11}BrO_4$ requires C, 46.15; H, 3.9%; $(M\text{-}H_2O)$ (^{79}Br), 267.9735); υ_{max}/cm^{-1} 3506 (OH), 1677 and 1652 (C=O) and 1589 and 1480 (C=C); δ_H 1.37 (3H, d, *J* 6.4 Hz, 3-CH_3), 1.47 (3H, d, *J* 6.9 Hz, 1-CH_3), 2.25 (1H, d, *J* 7.3 Hz, OH), 3.96 (1H, dq, *J* 2.2 and 6.4 Hz, 3-H), 4.35 (1H, dd, *J* 2.2 and 7.3 Hz, 4-H), 4.89 (1H, q, *J* 6.9 Hz, 1-H) and 7.32 (1H, s, 6-H); δ_C 16.1 (3-CH_3), 17.9 (1-CH_3), 61.1 (C-3), 66.4 (C-4), 67.6 (C-1), 137.6 (C-7), 137.8 (C-6), 139.2 (C-8a), 144.7 (C-4a), 178.6 (C-8), 183.7 (C-5); m/z 270 [M^+-H_2O (^{81}Br), 25%], 268 [M^+-H_2O (^{79}Br), 17%], 255 (100), 253 (80) and 149 (84). The product of lower R_F was identified as **60** (20 mg, 22%) m.p. 126-127 °C (hexane-dichloromethane) $[\alpha]_D$ +45.8 ° (*c* in 1.0 $CHCl_3$); (Found: C, 63.45; H, 5.8; M^+, 208.0734. $C_{11}H_{12}O_4$ requires C, 63.45; H, 5.8%; M, 208.0735); υ_{max}/cm^{-1} 3495 (OH) and 1655 (C=O); δ_H 1.37 (3H, d, *J* 6.4 Hz, 3-CH_3), 1.45 (3H, d, *J* 6.9 Hz, 1-CH_3), 2.22 (1H, br. s, OH), 3.97 (1H, dq, *J* 2.2 and 6.4 Hz, 3-H), 4.36 (1H, br. s, 4-H), 4.85 (1H, q, *J* 6.9 Hz, 1-H) and 6.75 and 6.80 (each 1H, d, *J* 10.8 Hz, 6- and 7-H); δ_C 16.1 (3-CH_3), 17.9 (1-CH_3), 61.1 (C-3), 66.5 (C-4), 67.0 (C-1), 136.3 (C-6), 136.8 (C-7), 138.6 (C-8a), 144.5 (C-4a), 186.3 (C-8) and 187.1 (C-5); m/z 190 [M^+-H_2O, 26%], 177 (19), 164 (100), 147 (21), 136 (56) and 119 (17).

(1*R*,3*S*,4*R*)-8-Benzyloxy-7-bromo-3,4-dihydro-4,5-dihydroxy-1,3-dimethyl-benzo[*c*]pyran 39 and **(1*R*,3*S*,4*S*)-8-Benzyloxy-7-bromo-3,4-dihydro-4,5-dihydroxy-3,4-dihydro-1,3-dimethylbenzo[*c*]pyran 44**

The (α′*R*, 2*S*) phenolic aldehyde **28** (200 mg, 0.53 mmol) was treated with titanium tetraisopropoxide (225 mg, 0.79 mmol) as described above for the phenolic aldehyde **25**, to afford the potentially unstable diols **39** and **44** as colourless oils in a ratio of 5:3 respectively. The product of higher R_F was identified as **39** (101 mg, 51%) $[\alpha]_D$ +46.2 ° (*c* 1.0 in $CHCl_3$); (Found: M^+, 378.0465. $C_{18}H_{19}BrO_4$ requires M(^{79}Br), 378.0466); υ_{max}(film)/cm^{-1} 3450 and 3292 (OH) and 1597 and 1461 (C=C); δ_H 1.39 (3H, d, *J* 6.1 Hz, 3-CH_3), 1.53 (3H, d, *J* 6.3 Hz, 1-CH_3), 3.39 (1H, dq, *J* 8.8 and 6.1 Hz, 3-H), 3.90-4.30 (2H, br. s, 4- and 5-OH), 4.55 (1H, dd, *J* 0.7 and 8.8 Hz, 4-H), 4.69 and 4.99 (each 1H, d, *J* 10.7 Hz, OCH_2), 4.76 (1H, dq, *J* 0.7 and 6.3 Hz, 1-H), 7.04 (1H, s, 6-H) and 7.34-7.49 (5H, m, C_6H_5); δ_C 17.9 (3-CH_3), 22.0 (1-CH_3), 71.0 (C-3), 71.9 (C-4), 73.5 (C-1), 75.0 (OCH_2), 117.5 (C-8), 119.6 (C-6), 122.5 (C-7), 128.4 (C-4″), 128.4 (C-2″ and C-6″), 128.5 (C-3″ and C-5″), 135.5 (C-1″), 136.6 (C-8a), 144.9 (C-4a) and 171.7 (C-5); m/z 362 [M^+-H_2O (^{81}Br), 8%], 360 [M^+-H_2O (^{79}Br), 8%], 255 (11), 149 (15), 91 (100) and 65 (16). The product of lower R_F was identified as **44** (60 mg, 30%) $[\alpha]_D$ +55.2 ° (*c* 1.0 in $CHCl_3$); (Found: C, 57.0; H, 5.2; M^+, 378.0465. $C_{18}H_{19}BrO_4$ requires C, 57.0; H, 5.05%; M(^{79}Br), 378.0466); υ_{max}(film)/cm^{-1} 3495 and 3265 (OH) and 1588 and 1495 (C=C); δ_H 1.34 (3H, d, *J* 6.5 Hz, 3-CH_3), 1.57 (3H, d, *J* 6.3 Hz, 1-CH_3), 3.59 (1H, dq, *J* 1.6 and 6.5 Hz, 3-H), 4.39 (1H, d, *J* 1.6 Hz, 4-H), 4.63 (1H, q, *J* 6.3 Hz, 1-H), 3.80-4.30 (2H, br. s, 4- and 5-OH), 4.71 and 4.97 (each 1H, d, *J* 10.7 Hz, OCH_2), 7.06 (1H, s, 6-H), 7.34-7.45 (5H, m, C_6H_5); δ_C 16.8 (3-CH_3), 21.9 (1-CH_3), 65.2 (C-3), 72.7 (C-4), 73.0 (C-1), 75.4 (OCH_2), 118.5 (C-8), 119.6 (C-6), 124.0 (C-7), 128.8 (C-4″), 128.9 (C-2″ and C-6″), 129.0 (C-3″ and C-5″), 136.0 (C-1″), 136.9 (C-8a), 146.0 (C-4a) and 152.3 (C-5);

m/z 363 [M^+-OH (^{81}Br), 16%], 361 [M^+-OH (^{79}Br), 16%], 255 (12), 253 (12), 205 (8), 149 (42), 84 (100) and 65 (10).

(1*R*,3*S*,4*R*)-7-Bromo-3,4-dihydro-4-hydroxy-1,3-dimethylbenzo[*c*]pyran-5-8-quinone 63 and (1*R*,3*S*,4*R*)-3,4-dihydro-4-hydroxy-1,3-dimethylbenzo[*c*]pyran-5-8-quinone 64

A solution of the diol **39** (55 mg, 0.15 mmol) in dry ethyl acetate (15 cm^3) was stirred with 10% palladium on carbon catalyst (55 mg) under a hydrogen atmosphere for 1.5 h. The mixture was filtered through celite, concentrated and purified through rapid chromatography (radial, 35% ethyl acetate-hexane) to afford the hydroquinonoid diols **40** and **41** as an unstable, oily mixture (42 mg, 0.15 mmol). This was immediately dissolved in acetonitrile (15 cm^3) and cerium(IV) ammonium nitrate (159 mg, 0.29 mmol) in water (3 cm^3) was added dropwise to the solution. After 20 min the reaction was quenched with water and exhaustively extracted with dichloromethane. The residue obtained upon work-up was chromatographed (radial, 15-25% ethyl acetate-hexane) to give the brominated quinone **63** and the debrominated quinone **64** as bright yellow crystals. The product of higher R_F was identified as **63** (18 mg, 43%), m.p. 116-118 °C (dichloromethane-hexane) $[\alpha]_D$ +349.4 ° (*c* in 1.0 $CHCl_3$); (Found: C, 46.45; H, 3.9; $(M-H_2O)^+$, 267.9724. $C_{11}H_{11}BrO_4$ requires C, 46.15; H, 3.9%; $(M-H_2O)(^{79}Br)$, 267.9735); υ_{max}/cm^{-1} 3226 (OH) and 1666 and 1652 (C=O); δ_H 1.41 (3H, d, *J* 6.2 Hz, 3-CH_3), 1.46 (3H, d, *J* 6.7 Hz, 1-CH_3), 3.41 (1H, dq, *J* 8.3 and 6.2 Hz, 3-H), 3.57 (1H, d, *J* 2.2 Hz, OH), 4.38 (1H, ddd, *J* 2.2, 2.9 and 8.3 Hz, 4-H), 4.70 (1H, dq, *J* 2.9 and 6.7 Hz, 1-H) and 7.25 (1H, s, 6-H); δ_C 18.2 (3-CH_3), 20.5 (1-CH_3), 67.6 (C-3), 70.5 (C-4), 73.0

(C-1), 137.8 (C-6), 138.0 (C-7), 140.8 (C-8a), 145.5 (C-4a), 178.8 (C-8) and 185.6 (C-5); m/z 288 [M^+ (^{81}Br), 100%], 286 [M^+ (^{79}Br), 98%], 215 (41), 213 (41), 164 (70), 136 (41), 107 (63), 77 (44) and 65 (20). The lower R_F product was identified as **64** (12 mg, 40%) and was obtained as an oil; (Found: $(M+2H)^+$, 210.0890. $C_{11}H_{12}O_4$ requires (M+2H), 210.0894). υ_{max}/cm^{-1} 3230 (OH) and 1672 and 1654 (C=O); δ_H 1.41 (3H, d, *J* 6.1 Hz, 3-CH_3), 1.45 (3H, d, *J* 6.7 Hz, 1-CH_3), 3.42 (1H, dq, *J* 8.3 and 6.1 Hz, 3-H), 3.69 (1H, d, *J* 2.0 Hz, OH), 4.38 (1H, ddd, *J* 2.0, 2.9 and 8.3 Hz, 4-H), 4.67 (1H, dq, *J* 2.9 and 6.7 Hz, 1-H) and 6.72 (2H, s, 6- and 7-H); δ_C 19.1 (3-CH_3), 21.4 (1-CH_3), 68.5 (C-3), 70.8 (C-4), 73.8 (C-1), 126.7 (C-8a), 136.9 (C-6), 138.0 (C-7, 141.0 (C-4a), 141.9 (C-8) and 186.3 (C-5); m/z 164 [M^+-CH_3CHO, 100%], 147 (12), 136 (51), 108 (51) and 91 (22).

(1*R*,3*S*,4*R*)-7-Bromo-3,4-dihydro-4-hydroxy-1,3-dimethylbenzo[*c*]pyran-5-8-quinone 63

Using tetrahydrofuran as solvent as described above in the conversion of diol **32** into its quinone **12**, the diol **39** was transformed into the quinone **63** as the sole product in a yield of 70%.

(1*R*,3*S*,4*S*)-7-Bromo-3,4-dihydro-4-hydroxy-1,3-dimethylbenzo[*c*]pyran-5,8-quinone 61 and (1*R*,3*S*,4*S*)-3,4-dihydro-4-hydroxy-1,3-dimethylbenzo[*c*]pyran-5,8-quinone 62

A solution of the diol **44** (110 mg, 0.29 mmol) in dry ethyl acetate (15 cm^3) was stirred with 10% palladium on carbon catalyst (110 mg) under a hydrogen atmosphere for 1.5 h. The mixture was filtered through celite, concentrated and purified through rapid

chromatography (radial, 35% ethyl acetate-hexane) to afford an unstable oily mixture **45** and **46** (80 mg, 0.28 mmol). This was immediately dissolved in acetonitrile (15 cm^3) and cerium(IV) ammonium nitrate (303 mg, 0.55 mmol) in water (3 cm^3) was added drop-wise to the solution. After 20 min the reaction was quenched with water and exhaustively extracted with dichloromethane. The residue obtained upon work-up was chromatographed (radial, 15-25% ethyl acetate-hexane) to give the brominated quinone **61** and the debrominated quinone **62** as bright yellow crystals. The product of higher R_F was identified as **61** (35 mg, 42%) m.p. 143-145 °C (dichloromethane-hexane) $[\alpha]_D$ +107 ° (*c* in 1.0 $CHCl_3$); (Found: C, 46.2; H, 3.8; $(M-H_2O)^+$, 267.9724. $C_{11}H_{11}BrO_4$ requires C, 46.15; H, 3.9%; $(M-H_2O)$ (^{79}Br), 267.9735); υ_{max}/cm^{-1} 3470 (OH) and 1672 and 1653 (C=O); δ_H 1.37 (3H, d, *J* 6.4 Hz, 3-CH_3), 1.54 (3H, d, *J* 6.6 Hz, 1-CH_3), 2.13 (1H, *J* 8.1 Hz, OH), 3.59 (1H, dq, *J* 1.6 and 6.4 Hz, 3-H), 4.37 (1H, ddd, *J* 1.4, 1.6 and 8.1 Hz, 4-H), 4.67 (1H, dq, *J* 1.4 and 6.6 Hz, 1-H) and 7.32 (1H, s, 6-H); δ_C 16.1 (3-CH_3), 20.6 (1-CH_3), 61.6 (C-3), 70.4 (C-4), 72.2 (C-1), 137.6 (C-6), 137.8 (C-7), 140.2 (C-8a), 145.4 (C-4a), 179.1 (C-8) and 183.3 (C-5); m/z 270 [M^+-H_2O (^{81}Br), 27%], 268 [M^+-H_2O (^{79}Br), 16%], 255 (100), 253 (71) and 149 (17). The product of lower R_F was identified as **62** (20 mg, 33%) as an orange oil; $[\alpha]_D$ -55.9 ° (*c* in 1.0 $CHCl_3$); (Found: C, 63.8; H, 5.6; $(M+2H)^+$, 210.0890. $C_{11}H_{12}O_4$ requires C, 63.45; H, 5.8%; (M+2H), 210.0892); υ_{max}/cm^{-1} 3569 (OH), 1655 (C=O) and 1602 (C=C); δ_H 1.37 (3H, d, *J* 6.4 Hz, 3-CH_3), 1.53 (3H, d, *J* 6.6 Hz, 1-CH_3), 2.08 (1H, br. s, OH), 3.59 (1H, dq, *J* 1.6 and 6.4 Hz, 3-H), 4.37 (1H, dd, *J* 1.4 and 1.6 Hz, 4-H), 4.64 (1H, dq, *J* 1.4 and 6.6 Hz, 1-H) and 6.73 and 6.80 (each 1H, d, *J* 10.2 Hz, 6- and 7-H); δ_C 16.1, (3-CH_3), 20.6 (1-CH_3), 61.6 (C-3), 69.9 (C-4), 73.3 (C-1), 136.0 (C-6), 137.1 (C-7), 139.7 (C-8a), 145.1 (C-4a),

185.9 (C-8) and 186.9 (C-5); m/z 164 [M^+-CH_3CHO, 100%], 147 (12), 136 (51), 108 (51) and 91 (22).

(1*R*,3*S*,4*S*)-7-Bromo-3,4-dihydro-4-hydroxy-1,3-dimethylbenzo[*c*]pyran-5,8-quinone 61

Using tetrahydrofuran as solvent as described above in the conversion of diol **32** into its quinone **12**, the diol **44** was transformed into the quinone **61** as the sole product in a yield of 77%.