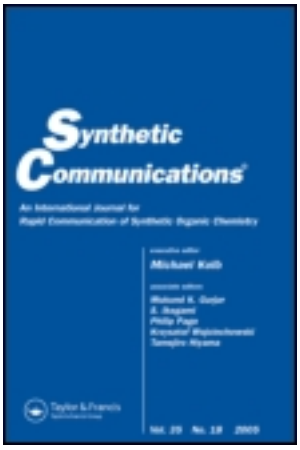


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# Oxidative Addition of 4-Hydroxycoumarin to Alkenes. An Expeditious Entry to 2,3-Dihydro-4H-furo-[3,2-c][1]benzopyran-4-ones[1]

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# OXIDATIVE ADDITION OF 4-HYDROXYCOUMARIN TO ALKENES. AN EXPEDITIOUS ENTRY TO 2,3-DIHYDRO-4*H*-FURO-[3,2-*c*][1]BENZOPYRAN-4-ONES[1]

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**ABSTRACT**. In the presence of one-electron metal oxidants (CAN, MAH), 4-hydroxycoumarin (**1**) adds to alkenes to give 2,3-dihydro-4*H*-furo[3,2-*c*][1]benzopyran-4-ones.

Over the past few years, considerable attention has been given to the oxidative addition of active methylene compounds to alkenes.[2] When β-diketones and β-keto esters are employed, dihydrofuran adducts are obtained from a variety of electron-rich alkenes.[3] The reaction is promoted by one-electron metal oxidants like cerium (IV) ammonium nitrate (CAN)[4] or manganese (III) acetate hydrate (MAH),[5] and is triggered by the oxidation of the carbonyl substrate to an electrophilic α-oxo alkyl radical. The latter then adds to the olefin double bond, generating a nucleophilic

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alkyl radical (Figure 1). The exact mechanistic details and the sequence of the following steps remain unclear, and might differ (Path A or B) according to the oxidant employed, since CAN and MAH have different oxidizing capacity toward alkyl radicals.[6]

The reaction has great potential, and has been exploited for the synthesis of complex natural products.[3] Surprisingly, no example with the natural compound 4-

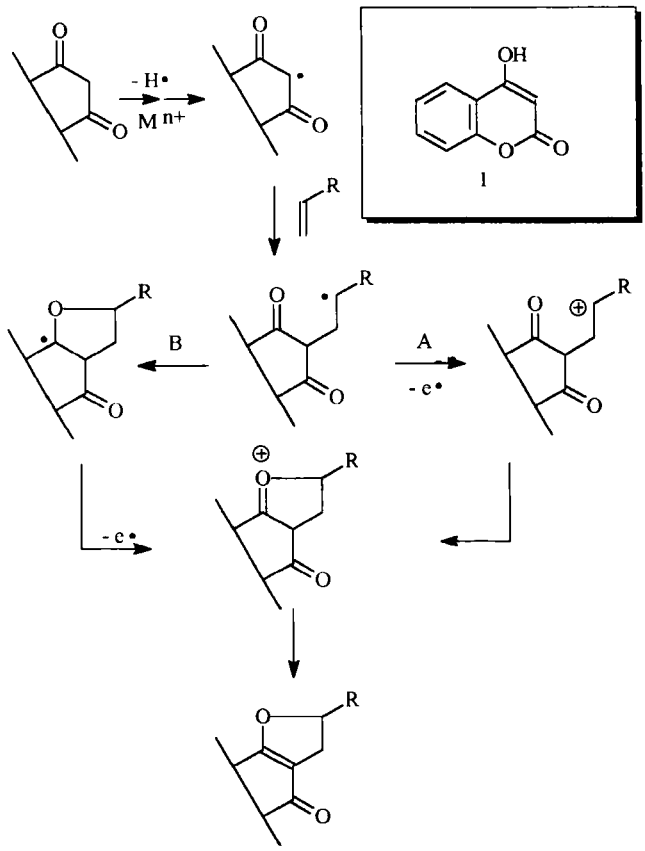



**FIG.1**

hydroxycoumarin (**1**) as the active methylene compound has been reported, despite the widespread occurrence of this moiety within secondary metabolites of plant and fungal origin, and the continual attention received by the biological activity of coumarin derivatives.[7]

In preliminary experiments, **1** was treated with CAN or MAH and a series of alkenes (Table, Entries 1, 5, 8, 9). Both oxidants gave the same reaction products, but CAN was superior in terms of work-up practicity and yield. Furthermore, the reaction could be carried out with a near equimolecular ratio between **1** and the olefin substrate, avoiding the excess of alkene necessary with MAH. CAN was thus used to extent the reaction to a series of other unsaturated substrates (Table). In most cases, only angular adducts were obtained, but tiglol and methallyl alcohol gave a near equimolecular mixture of linear and angular adducts (Table, Entries 2 and 3). The linear adducts are the result of the oxidative trapping of the nucleophilic addition radical by the ester carbonyl. This is surprising and unprecedented in the oxidative addition of β-keto esters to alkenes, since ketone carbonyls are better radical- and cation sink than ester carbonyls.[3,5]

Interestingly, cationic rearrangements of the terpene moiety and formation of nitrate esters, both documented in this type of oxidative additions,[8,9] were not observed, suggesting that intramolecular oxygen trapping of cationic (radical) intermediates is faster than skeletal rearrangement or nitrate trapping. Diastereoselection was excellent with α-pinene and limonene, as shown by the obtaining of the stereochemically homogeneous adducts **4** and **6**, respectively. However, β-pinene gave a mixture of diastereomers (**5a,b**).

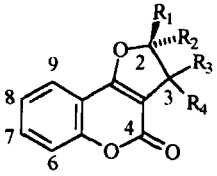
**Table. Oxidative addition of 4-hydroxycoumarin to alkenes**

| Entry | Alkene | Method* | Rxn.Time (h) | Product(s) (Yield %) |
|---|---|---|---|---|
| 1. | Tetramethylethylene | A<br>B | 4<br>10 | **2a** (42)<br>**2a** (33) |
| 2. | 2-Methyl-2-propen-1-ol (= methallyl alcohol) | A | 3 | **2b**(23),<br>**3a** (24) |
| 3. | *E*-2-Methyl-2-buten-1-ol (= tiglol) | A | 4 | **2c**(32),<br>**3b** (32) |
| 4. | Isopropenyl acetate | A | 5 | **2d** 10) |
| 5. | α-Methylstyrene | A<br>B | 16<br>20 | **2e** (46)<br>**2e** (35) |
| 6. | *E*–β-Methylstyrene | A | 16 | **2f** (46) |
| 7. | Methyl cinnamate | A | 24 | **2g** (25) |
| 8. | (1*S*) (-) α-Pinene | A<br>B | 4<br>6 | **4** (94)<br>**4** (72) |
| 9. | (1*S*) (-) β-Pinene | A<br>B | 3<br>4 | **5a,b** (7)<br>**5a,b** (9) |
| 10. | (*R*) (+) Limonene | A | 6 | **6** (57) |

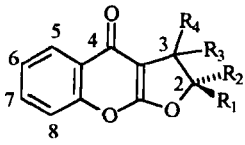
* A: CAN-oxidation; B: MAH -oxidation

With 1,2-disubstituted alkenes (*E*- β-methylstyrene, *E*-methyl cinnamate) only *trans*-disubstituted adducts were obtained (**2f** and **2g**, respectively), but the trisubstituted olefin tiglol gave a mixture of *cis*- and *trans* disubstituted adducts (Table, Entry 3).

In conclusion, the CAN-induced oxidative addition of 4-hydroxycoumarin to alkenes represents a new and straightforward method for the synthesis of 2,3-dihydro-4*H*-furo[3,2-*c*][1] benzopyran-4-ones, superior in terms of versatility to the existent procedures.[10] A wide variety of substitution and functionality patterns can be accessed quickly. The reaction has thus great potential for natural products synthesis, since many meroterpenoids with a 2,3-disubstituted dihydrofurano[3,2-*c*]coumarin core are known.[11]

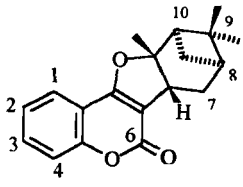


| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| **2a** | Me | Me | Me | Me |
| **2b** | $CH_2OH$ | Me | H | H |
| **2c**[a] | $CH_2OH$ | Me | Me | H |
| **2d** | $CH_3$ | - | - | H $\Delta^{2,3}$ |
| **2e** | Ph | Me | H | H |
| **2f**[b] | Ph | H | Me | H |
| **2g**[b] | Ph | H | H | COOMe |

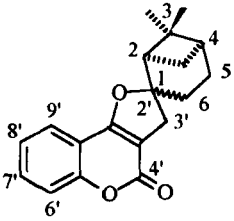


| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| **3a** | $CH_2OH$ | Me | H | H |
| **3b**[a] | $CH_2OH$ | Me | Me | H |

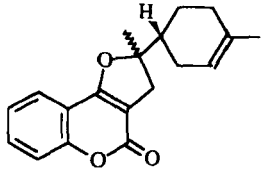
a: *cis/trans* mixture (*ca* 3:2)
b: *trans* isomer



**4**



**5a:** 2'(1)*R*
**5b:** 2'(1)*S*



**6**

## Experimental

Melting points are uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AC-300 spectrometer at 300 and 75 MHz, respectively. All solvents and chemicals were reagent grade. Tiglol was prepared from tiglic acid according to literature.[12]

*Oxidative Addition of 4-Hydroxycoumarin to Alkenes*:

a) CAN as oxidant: to a suspension of **1** in acetonitrile (25 ml/ g of **1**), the unsaturated substrate (0.8 equiv.) was added, and a solution of CAN (2.2 equiv.) in acetonitrile (10 ml/g of CAN) was added dropwise. The reaction was stirred at room temp. until completion (disappearance of the olefin and decoloration), and

worked up by concentration, dilution with water and extraction with EtOAc. The organic phase was washed with sat. $Na_2CO_3$ to remove unreacted **1**, and evaporated. The residue was purified by trituration with ether (compounds **2a**, **4**, **6**) or by chromatography (hexane-EtOAc mixtures) followed by trituration with ether. When a mixture was obtained, the linear and the angular adducts could be easily separated by column chromatography on silica gel, using mixtures of hexane-EtOAc as eluant (hexane-EtOAc 3:7 for the separation of **2b** and **3a**; hexane-EtOAc 1:9 for the separation of **2c** and **3b**). The angular adduct was always the least polar, and was eluted before the linear one.

b) MAH as oxidant: to a suspension of **1** in HOAc (*ca* 60 ml/g of **1**), the unsaturated substrate (5 equiv.) and $Mn(OAc)_3.2H_2O$ (5 equiv.) were added. The mixture was stirred at 90° until completion (disappearance of **1** and change of colour), diluted with water and extracted with hexane-EtOAc 1:1. The organic phase was washed with sat. $Na_2CO_3$ and further processed as described for the CAN- oxidations.

*Structure Elucidation.* $^{13}$C-NMR spectra were fully assigned using two-dimensional techniques [$^2$J and $^3$J (HMBC) $^1$H-$^{13}$C correlations]. Systematic numbering[13] was used for the assignment of the $^1$H- and $^{13}$C-NMR spectra. The stereochemistry of **4** was confirmed by X-ray analysis. For a general discussion of the spectroscopic differentiation of linear and angular adducts, see ref. 14.

**2a**: Mp: 90 °C; IR (KBr): 1710, 1640, 1605, 1568, 1400, 1088, 988, 960, 783 cm$^{-1}$; MS(EI): 244 ($C_{15}H_{16}O_3^+$, $M^+$) (10), 229 (100); $^1$H-NMR ($CDCl_3$): δ 7.62 (br d, J=8.0 Hz, H-9), 7.51 (br t, J=8.0 Hz, H-7), 7.32 (br d, J=8.0 Hz, H-6), 7.23 (br t, J=8.0 Hz, H-8), 1.32 (s, 3-Me), 1.43 (s, 2-Me); $^{13}$C-NMR ($CDCl_3$): δ 96.0 (s, C-

2), 45.9 (s, C-3), 110.0 (s, C-3a), 160.3 (s, C-4), 154.9 (s, C-5a), 116.7 (d, C-6), 131.9 (d, C-7), 123.6 (d, C-8), 122.7 (d, C-9), 132.2 (s, C-9a), 164.0 (s, C-9b), 23.0 (q, 2-Me), 21.8 (q, 3-Me).

**2b**: Mp: 138 °C; IR(KBr): 3436, 1694, 1640, 1500, 1418, 1383, 1109, 955, 897, 770 $cm^{-1}$; MS(EI): 232 ($C_{13}H_{12}O_4^+$, $M^+$) (100); $^1$H-NMR ($CDCl_3$): δ 7.60 (br d, J=8.0 Hz, H-9), 7.52 (br t, J=8.0 Hz, H-7), 7.33 (br d, J=8.0 Hz, H-6), 7.25 (br t, J=8.0 Hz, H-8), 3.77 (d, J=12.4 Hz, 2-$CH_2$OH), 3.70 (d, J=12.4 Hz, 2-$CH_2$OH), 3.20 (d, J=14.2 Hz, H-3a), 2.83 (d, J=14.2 Hz, H-3b), 1.53 (s, 2-Me); $^{13}$C-NMR ($CDCl_3$): δ 94.7 (s, C-2), 34.8 (d, C-3), 102.0 (s, C-3a), 160.8 (s, C-4), 154.8 (s, C-5a), 116.9 (d, C-6), 132.2 (d, C-7), 123.8 (d. C-8), 122.7 (d, C-9), 112.6 (s, C-9a), 165.7 (s, C-9b), 67.9 (t, 2-$CH_2$OH), 23.4 (q, 2-Me).

**2c**: Mp 110°C; IR(KBr): 3486, 1689, 1643, 1520, 1412, 1086, 1063, 986, 820 $cm^{-1}$; MS(EI): 246 ($C_{14}H_{14}O_4^+$, $M^+$) (89), 215 (100); $^1$H-NMR ($CDCl_3$): δ (*cis*-isomer) 7.60 (br d, J=8.0 Hz, H-9), 7.47 (br t, J=8.0 Hz, H-7), 7.26 (br d, J=8.0 Hz, H-6), 7.17 (br t, J=8.0 Hz, H-8), 3.67 (br s, 2-$CH_2$OH), 3.88 (q, J=6.8 Hz, H-3), 1.44 (s, 2-Me), 1.27 (d, J=6.8 Hz, 3-Me); (*trans*-isomer) 7.63 (br d, J=8.0 Hz, H-9), 7.48 (br t, J=8.0 Hz, H-7), 7.27 (br d, J=8.0 Hz, H-6), 7.18 (br t, J=8.0 Hz, H-8), 3.91 (d, J=12.0 Hz, 2-$CH_2$OH), 3.76 (d, J=12.0 Hz, 2-$CH_2$OH), 3.27 (q, J=6.8 Hz, H-3), 1.51 (s, 2-Me), 1.33 (d, J=6.8 Hz, 3-Me); $^{13}$C-NMR ($CDCl_3$): δ (*cis*-isomer) 96.7 (s, C-2), 38.8 (d, C-3), 106.7 (s, C-3a), 160.8 (s, C-4), 154.8 (s, C-5a), 116.7 (d, C-6), 132.1 (d, C-7), 123.7 (d, C-8), 122.7 (d, C-9), 112.7 (s, C-9a), 164.8 (s, C-9b), 17.6 (q, 2-Me), 68.0 (t, 2-$CH_2$OH), 13.5 (q, 3-Me); (*trans*-isomer) 96.5 (s, C-2), 43.5 (d, C-3), 106.7 (s, C-3a), 160.8 (s, C-4), 154.8 (s, C-

5a), 116.7 (d, C-6), 132.1 (d, C-7), 123.7 (d, C-8), 122.7 (d, C-9), 112.7 (s, C-9a), 164.0 (s, C-9b), 23.6 (q, 2-Me), 64.9 (t, 2-$CH_2OH$), 12.5 (q, 3-Me).

**2d**: Mp: 150°C; IR(KBr): 1728, 1632, 1589, 1501, 1361, 1101, 974, 928, 758 $cm^{-1}$; MS(EI): 200 ($C_{12}H_{10}O_3^+$, $M^+$) (100); $^1$H-NMR ($CDCl_3$): δ 7.81 (br d, J=8.0 Hz, H-9), 7.47 (br t, J=8.0 Hz, H-7), 7.41 (br d, J=8.0 Hz, H-6), 7.33 (br t, J=8.0 Hz, H-8), 6.57 (s, H-3), 2.49 (s, 2-Me).

**2e**: Mp: 105°C; IR(KBr): 1717, 1647, 1607, 1580, 1412, 1281, 1034, 754, 706 $cm^{-1}$; MS(EI): 278 ($C_{18}H_{14}O_3^+$, $M^+$) (50), 158 (100); $^1$H-NMR (DMSO-$d_6$): δ 7.77 (br d, J=8.0 Hz, H-9), 7.67 (br t, J=8.0 Hz, H-7), 7.45 (br d, J=8.0 Hz, H-6), 7.51 (m, *o*-Ph), 7.40 (m, *m*-Ph), 7.37 (br t, J=8.0 Hz, H-8), 7.31 (m, *p*-Ph), 3.33 (d, J=14.2 Hz, H-3a), 3.21 (d, J=14.2 Hz, H-3b), 1.85 (s, 2-Me); $^{13}$C-NMR (DMSO-$d_6$): δ 94.4 (s, C-2), 40.9 (t, C-3), 101.0 (s, C-3a), 159.0 (s, C-4), 154.3 (s, C-5a), 116.4 (d, C-6), 132.5 (d, C-7), 124.1 (d, C-8), 122.4 (d, C-9), 112.0 (s, C-9a), 164.1 (s, C-9b), 28.5 (q, 2-Me), 144.5 (s, *i*-Ph), 124.1 (d, *o*-Ph), 128.4 (d, *m*-Ph), 127.6 (d, *p*-Ph).

**2f**: Mp: 47°C; IR(KBr): 1707, 1645, 1605, 1566, 1497, 1412, 928, 754, 698 $cm^{-1}$; MS(EI): 278 ($C_{18}H_{14}O_3^+$, $M^+$)(20), 158 (100); $^1$H-NMR ($CDCl_3$): δ 7.73 (br d, J=8.0 Hz, H-9), 7.58 (br t, J=8.0 Hz, H-7), 7.36 -7.27 (overlapped m, Ph), 5.49 (d, J=7.2 Hz, H-2), 3.58 (m, H-3), 1.56 (d, J=6.3 Hz, 3-Me).

**2g**: Mp: 138°C; IR(KBr): 1726, 1638, 1605, 1566, 1414, 1258, 1120, 924, 761 $cm^{-1}$;MS(EI): 322 ($C_{19}H_{14}O_5^+$, $M^+$)(38), 263 (100); $^1$H-NMR ($CDCl_3$): δ 7.74 (br d, J=8.0 Hz, H-9), 7.61 (br t, J=8.0 Hz, H-7), 7-41-7.31 (m, 2-Ph), 7.40 (br d, J=8.0 Hz, H-6), 7.31 (br t, J=8.0 Hz, H-8), 6.22 (d, J=6.8 Hz, H-2), 4.31 (d, J=6.8

Hz, H-3), 3.83 (s, 2-COOMe); $^{13}$C-NMR ($CDCl_3$): 90.6 (d, C-2), 53.5 (d, C-3), 100.7 (s, C-3a), 159.0 (s, C-4), 155.4 (s, C-5a), 117.1 (d, C-6), 133.2 (d, C-7), 124.2 (d, C-8), 123.2 (d, C-9), 112.0 (s, C-9a), 166.7 (s, C-9b), 138.4 (s, *i*-Ph), 125.5 (d, *o*-Ph), 129.1 (d, *m*-Ph), 129.3 (d, *p*-Ph).

**3a**: Mp: 147°C; IR(KBr): 3390, 1613, 1558, 1461, 1419, 1283, 1165, 1073, 756 cm$^{-1}$; MS(EI): 232 ($C_{13}H_{12}O_4^+$, $M^+$) (80), 121 (100); $^1$H NMR ($CDCl_3$): δ 8.16 (d, J=8.0 Hz, H-5), 7.55 (br t, J=8.0 Hz, H-7), 7.35 (br t, J=8.0 Hz, H-6), 7.33 (br d, J=8.0 Hz, H-8), 3.76 (d, J=12.6 Hz, 2-$CH_2$OH), 3.70 (d, J=12.6 Hz, 2-$CH_2$OH), 3.23 (d, J=14.6 Hz, H-3a), 2.85 (d, J=14.6 Hz, H-3b), 1.53 (s, 2-Me). $^{13}$C-NMR ($CDCl_3$): δ 93.4 (s, C-2), 33.1 (t, C-3), 95.2 (s, C-3a), 175.3 (s,, C-4), 123.6 (s, C-4a), 125.5 (d, C-5), 125.8 (d, C-6), 132.4 (d, C-7), 117.3 (d, C-8), 153.3 (s, C-8a), 168.0 (s, C-9a), 67.8 (t, 2-CH2OH), 23.2 (q, 2-Me).

**3b**: Mp 119°C; IR(KBr): 3347, 1609, 1557, 1480, 1462, 1368, 1072, 758 cm$^{-1}$; MS(EI): 246 ($C_{14}H_{18}O_4^+$, $M^+$), 189 (100); $^1$H-NMR ($CDCl_3$): δ (*cis*-isomer) 8.08 (br d, J=8.0 Hz, H-5), 7.50 (br t, J=8.0 Hz, H-7), 7.30 (br t, J=8.0 Hz, H-6), 7.30 (br d, J=8.0 Hz, H-8), 3.67 (br s, 2-$CH_2$OH), 3.49 (q, J=6.8 Hz, H-3), 1.43 (s, 2-Me), 1.30 (d, J=6.8 Hz, 3-Me); (*trans*-isomer) 8.11 (br d, J=8.0 Hz, H-5), 7.50 (br t, J=8.0 Hz, H-7), 7.30 (br t, J=8.0 Hz, H-6), 7.30 (br d, J=8.0 Hz, H-8), 3.93 (d, J=12.2 Hz, 2-$CH_2$OH), 3.73 (d, J=12.2 Hz, 2-$CH_2$OH), 3.36 (q, H-3), 1.52 (s, 2-Me), 1.39 (d, J=6.8 Hz, 3-Me); $^{13}$C-NMR ($CDCl_3$): δ (*cis*-isomer) 95.6 (s, C-2), 37.5 (d, C-3), 99.8 (s, C-3a), 175.4 (s, C-4), 124.0 (s, C-4a), 125.5 (d, C-5), 125.4 (d, C-6), 132.0 (d, C-7), 117.2 (d, C-8), 153.2 (s, C-8a), 167.7 (s, C-9a), 17.0 (q, 2-Me), 67.9 (t, 2-$CH_2$OH), 14.0 (q, 3-Me); (*trans*-isomer) 95.0 (s, C-2), 42.2 (d,

C-3), 99.7 (s, C-3a), 175.0 (s, C-4), 123.7 (s, C-4a), 125.5 (d, C-5), 125.4 (d, C-6), 132.0 (d, C-7), 117.2 (d, C-8), 153.2 (s, C-8a), 167.7 (s, C-9a), 13.0 (2-Me), 64.6 (t, 2-$CH_2OH$), 23.0 (q, 3-Me).

**4**: Mp: 210°C; IR(KBr):1720, 1643, 1603, 1566, 1499, 1400, 1015, 812, 764 $cm^{-1}$; MS(EI): 296 ($C_{19}H_{20}O_3^+$, $M^+$)(13), 108 (100); $^1$H-NMR ($CDCl_3$): 7.64 (br d, J=8.0 Hz, H-1), 7.51 (br t, J=8.0 Hz, H-3), 7.34 (br d, J=8.0 Hz, H-4), 7.24 (br t, J=8.0 Hz, H-2), 3.30 (dd, J=10.0, 6.2 Hz, H-6b), 2.40 (m, H-7), 2.28 (dd, J=7.0, 6.0 Hz, H-10), 2.23 (m, H-12), 1.97 (m, H-8), 1.94 (m, H-7'), 1.50 (s, 10a-Me), 1.30 (s, 9-αMe), 1.03 (m, H-12'), 0.97 (s, 9-βMe); $^{13}$C-NMR ($CDCl_3$): δ 123.0 (d, C-1), 123.7 (d, C-2), 132.0 (d, C-3), 116.8 (d, C-4), 154.9 (s, C-4a), 164.3 (s, C-6), 107.2 (s, C-6a), 39.1 (d, C-6b), 31.8 (t, C-7), 39.2 (d, C-8), 38.2 (s, C-9), 50.8 (d, C-10), 99.7 (s, C-10a), 26.0 (t, C-12), 23.0 (q, 9-βMe), 27.0 (q, 9-αMe), 27.5 (q, 10a-Me).

**5a,b**: Mp: 167°C; IR(KBr): 1713, 1643, 1500, 1408, 1030, 895, 752 $cm^{-1}$; MS(EI): 296 ($C_{19}H_{20}O_3^+$, $M^+$) (6), 175 (100); $^1$H-NMR ($CDCl_3$) (isomer ratio *ca* 2:1): major isomer: δ 7.50 (br t, J=8.0 Hz, H-9'), 7.37 (br d, J=8.0 Hz, H-7'), 7.34 (br d, J= 8.0 Hz, H-6'), 7.27 (br t, J= 8.0 Hz, H-8'), 3.09 (d, J=14.2 Hz, H-3'a), 3.02 (d, J=14.2 Hz, H-3'b), 2.50 (m, H-6a), 2.31 (m, H-3a), 2.22 (m, H-2), 2.15 (m, H-5a), 2.06 (m, H-6b), 2.03 (m, H-4), 1.93 (m, H-5b), 1.67 (m, H-3b), 1.27 (s, 7-Me), 0.98 (s, 7-Me); minor isomer: δ 7.60 (br d, J=8.0 Hz, H-9'), 7.53 (br t, J=8.0 Hz, H-7'), 7.34 (br d (J=8.0 Hz, H-6'), 7.24 (br t, J=8.0 Hz, H-8'), 3.09 (d, J=14.2 Hz, H-3'a), 3.05 (d, J=14.2 Hz, H-3'b), 2.43 (m, H-6a), 2.35 (m, H-3a), 2.22 (m, H-2), 2.15 (m, H-5a), 2.06 (m, H-6b), 2.03 (m, H-4), 1.93 (m, H-5b),

1.16 (m, H-3b), 1.23 (s, 7-Me), 1.18 (s, 7-Me ). $^{13}$C-NMR (CDCl3): δ (major isomer) 100.4 (s, C-2'), 42.3 (t, C-3'), 101.4 (C-3a'), 160.9 (s, C-4), 154.9 (s, C-5a'), 116.9 (d, C-6'), 132.0 (d, C-7'), 123.6 (d, C-8'), 122.8 (d, C-9'), 112.9 (s. C-9a'), 164.7 (s, C-9b'), 57.6 (d, C-2), 26.5 (t, C-3), 40.0 (d, C-4), 24.1 (t, C-5), 31.8 (t, C-6), 38.3 (s, C-7), 22.9 (q, 7-Me), 26.8 (q, 7-Me); δ (minor isomer) 100.2 (s, C-2'), 42.6 (t, C-3'), 100.6 (s, C-3a'), 160.9 (s, C-4), 154.9 (s, C-5a'), 116.9 (d, C-6'), 132.0 (d, C-7'), 123.6 (d, C-8'), 122.7 (d, C-9'), 113.0 (s. C-9a'), 165.5 (s, C-9b'), 51.4 (d, C-2), 27.1 (t, C-3), 40.1 (d, C-4), 24.1 (t, C-5), 31.4 (t, C-6), 38.2 (s, C-7), 23.4 (q, 7-Me), 27.0 (q, 7-Me);

**6**: Mp:130°C; IR(KBr): 1728, 1647, 1500, 1412, 1032, 750, 733 cm$^{-1}$; MS(EI): 296 ($C_{19}H_{20}O_3^+$, $M^+$) (20), 134 (100); $^1$H-NMR ($CDCl_3$): δ 7.64 (br d, J=8.0 Hz, H-9), 7.52 (br t, H=8.0 Hz, H-7), 7.34 (br d, J=8.0 Hz, H-6), 7.25 (br t, J=8.0 Hz, H-8), 5.39 (br s, H-3'), 3.08 (d, J=15.0 Hz, H-3a), 2.73 (d, J=15.0 Hz, H-3b), 2.13 (m, H-2'a), 2.00 (m, H-1'), 1.93 (m, H-5'a,b), 1.87 (m, H-2'b), 1.75 (m, H-6'a), 1.63 (s, 2-Me), 1.50 (s, 4'-Me), 1.31 (m, H-6'b); $^{13}$C-NMR ($CDCl_3$): δ 97.7 (s, C-2), 35.6 (t, C-3), 101.4 (s, C-3a), 164.4 (s, C-4), 154.9 (s, C-5a), 116.9 (d, C-6), 132.1 (d, C-7), 123.7 (d, C-8), 122.7 (d, C-9), 112.8 (s, C-9a), 160.9 (s, C-9b), 24.7 (q, 2-Me), 43.1 (d, C-1'), 26.3 (t, C-2'), 119.5 (d, C-3'), 134.1 (s, C-4'), 30.2 (t, C-5'), 23.4 (t, C-6'), 23.3 (q, 4'-Me).

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