CONSTITUENTS OF WEST AFRICAN MEDICINAL PLANTS XVIII[1]: THE ANNONIDINES - A NEW CLASS OF PRENYLATED BISINDOLE ALKALOIDS FROM ANNONIDIUM MANNII

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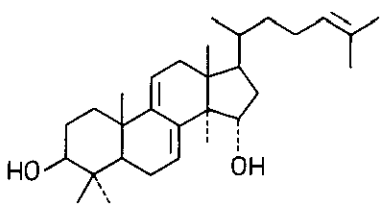
Abstract ——— From the stem bark of Annonidium mannii annonidines A - E (3 - 7) have been isolated and their structures determined. 3 to 7 belong to a new structural type of prenylated bisindole alkaloids.

The stem bark of the West African Annonidium mannii Engl. & Diels (Annonaceae)[2] was extracted with petroleum ether; on concentration large quantities of polycarpol (1)[3] precipitated and were removed. The better soluble constituents were subjected to column chromatography, and this yielded 7-(3-methyl-2-butenyl)-indole (2)[4] and the hitherto unknown prenylated bisindole alkaloids 3 to 7. Since these compounds constitute a new group of bisindole alkaloids they were named annonidines.



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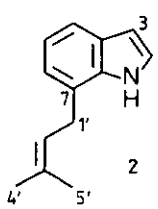

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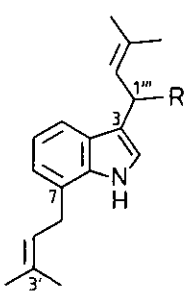
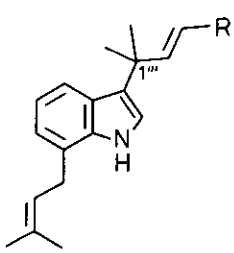
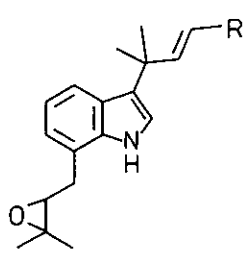






3: R = 7-indolyl

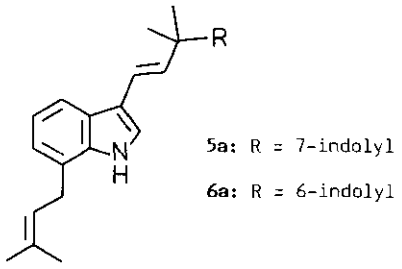
4: R = 3-indolyl

5: R = 7-indolyl

6: R = 6-indolyl

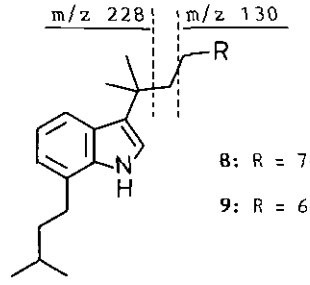
7: R = 7-indolyl

Structure determination is based on ^{1}H- (at 400 MHz) and ^{13}C-NMR measurements and on UV- and MS-investigations of the original alkaloids and partly their hydrogenation derivatives. The spectra show, that in all compounds two indole systems are present and these are linked together by an isoprenoid C_5-unit. In annonidines A and B (**3** and **4**) both indoles are connected to C-1 of a 3-methyl-2-butene, whereas in annonidines C to E (**5** to **7**) the indoles are bound at C-1 and C-3 of a 3-methyl-1-butene. Another 3-methyl-2-butenyl unit is observed in **3** to **6** as a substituent of one of the indole nuclei. This C_5-substituent must be localized at C-7 of the indole; besides other arguments evidence comes from the ^{13}C-NMR resonances of the methylene carbon atoms which appear at δ = 31 ppm; in case of substitution at C-3 δ = 24 ppm and at C-6 δ = 35 ppm would be typical values[5]. From analysis of the ^{13}C-signals of the indole carbon atoms the other positions of substitution can be determined and this is particularly easy, if C-3 or C-7 are involved, since the resonances of these carbon atoms if unsubstituted appear typically at highest field (δ_{C-3} = 103 ppm; δ_{C-7} = 111 ppm)[5,6]. Only annonidine D (**6**) contains an indole substituted at C-6 and this was deduced from the ^{1}H-NMR and a singlet at δ = 132.5 ppm in the ^{13}C-NMR. The data mentioned above allow to establish structures **3** and **4** for annonidines A and B unambiguously; but for annonidines C and D (**5** and **6**) still exist the alternative formulae **5a** and **6a**. Therefore **5** and **6** were hydrogenated to give their tetrahydro derivatives **8** and **9** , whose MS - fragmentation exhibit key fragments at m/z 228 and m/z 130 and thus exclude structures **5a** and **6a**.



5a: R = 7-indolyl

6a: R = 6-indolyl



8: R = 7-indolyl

9: R = 6-indolyl

The ^{1}H- and ^{13}C-NMR of annonidine E (**7**) show close similarity with the spectra of **5** for all signals except for C-7 of the disubstituted indole nucleus and the C_5-unit attached to that carbon atom. However, the resonances of this substituent and all other data fit completely to an epoxidized prenyl group[5] and therefore establish formula **7** for annonidine E.

From a biogenetic point of view **3**, **5** and **7** can be regarded as dimeric 7-prenylindoles (dimerization products of **2**), whereas for the formation of **4** and **6** various pathways might be possible.

Polycarpol (**1**) has exclusively be isolated from some plants of the Annonaceae family[7]; 7-(3-methyl-2-butenyl)-indole (**2**) up-to-now has been only described from the liverworts Riccardia sinuata and R. incurvata[4].

EXPERIMENTAL

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Optical rotations were measured in $CHCl_3$; IR in KBr, UV in EtOH. NMR spectra were recorded in $CDCl_3$ using tetramethylsilane as the internal reference on a Jeol GX-400 spectrometer (^1H at 400 MHz, if not stated otherwise) and on a Jeol FX-90 Q instrument (^1H at 90 MHz and ^{13}C at 22.5 MHz); compounds 3 to **9** were numbered in the following manner: C-2 to C-7a for the disubstituted indole, C-1' to C-5' for the substituent at C-7, C-2" to C-7a" for the monosubstituted indole and C-1"' to C-5"' for the connecting substituent. Mass spectra were obtained at 70 eV on a Finnigan 4000 instrument and on a Varian MAT 311 A spectrometer (high resolution MS data). Ready made Nano-plates SIL-20 UV_{254} (Macherey-Nagel) were used for TLC; detection by spraying with anisaldehyde (reagent No. 15 according to Stahl[8]); standard solvent system was petroleum ether (bp 65-70°C)/ethyl acetate (9:1).

Plant material ——— *Annonidium mannii* was collected at Bobiri Forest Reserve (near Kumasi, Ghana) in November 1984 by Mr. A. A. Enti (Forestry Enterprises, Accra, Ghana). A voucher specimen (No. 8407) is deposited in our herbarium.

Extraction and separation ——— Dried ground stem bark (2 kg) was percolated at 20°C with 35 l of petroleum ether (bp 65-70°C). The solvent was evaporated under reduced pressure (220 hPa; water bath temperature 40-50°C). During concentration of the extract to 300 ml a precipitate was formed, which was filtered off to give 7.5 g of crude polycarpol (**1**).

The filtrate was evaporated further yielding an oily red residue (5 g), which was subjected to column chromatography on silica gel 60 (0.04-0.063 mm, Macherey-Nagel). Elution with petroleum ether (bp 65-70°C)/ethyl acetate (increasing the concentration of ethyl acetate from 10 to 90%) gave fractions P_1 to P_{19}. Fraction P_3 (350 mg), P_6 (220 mg), P_8 (240 mg), P_{10} (135 mg), P_{12} (410 mg) and P_{14} (62 mg) were separated by column chromatography on Fractogel PVA 500 (Merck) using either methanol or ethanol as the eluent and this yielded the pure compounds **2** to **7**.

Polycarpol (**1**) ——— Crystallization from methanol gave colorless needles, mp 172-174°C (lit.[3]: mp 173-174°C), $[\alpha]_D^{20}$ = +93° (c = 1.0) (lit.[3]: $[\alpha]_D$ = +90°). All spectra (IR, UV, ^1H-NMR and MS) were in full accordance with the published data[3,9].

7-(3-Methyl-2-butenyl)-indole (**2**) ——— Chromatography of fraction P_3 (3 x 115 mg) on PVA 500 (15 g each, ethanol) yielded crystalline **2** (240 mg), mp 43-44°C (lit.[4]: mp ≈ 20°C). TLC: Rf = 0.37, anisaldehyde: orange; IR: ν_{max} = 3390 (NH), 1435, 792, 728 cm^{-1}; UV: λ_{max}(log ε) = 219 (4.59), 270 (3.87), 288 nm (3.68); MS: m/z (rel. int.) = 185 (100%, M^+), 170 (99), 155 (22),

130 (77), 117 (29); ^{1}H-NMR (90 MHz): δ (ppm) = 8.12 (br s; 1H, NH), 7.51 (m; 1H, 4-H), 7.18 (dd, J_1= 3.2 Hz, J_2= 2.5 Hz; 1H, 2-H), 7.02 (m; 2H, 5-H and 6-H), 6.56 (dd, J_1= 3.2 Hz, J_2= 2.2 Hz; 1H, 3-H), 5.42 (tqq, J_1= 7.1 Hz, J_2= J_3= 1.5 Hz; 1H, =CH-CH_2), 3.57 (br d, J = 7 Hz; 2H, =CH-CH_2), 1.81 and 1.78 (2 x s; 6H, =C(CH_3)$_2$); ^{13}C-NMR: δ = 135.0 (s; C-7a), 133.1 (s; C-3'), 127.8 (s; C-3a), 123.9 (s; C-7), 123.8 (d; C-2), 122.1 (d; C-2'), 121.3, 119.9 and 118.6 (3 x d; C-6, C-5, C-4), 102.8 (d; C-3), 30.5 (t; C-1'), 25.6 (q; C-4'), 17.8 (q; C-5').

Annonidine A = 3-[1-(7-Indolyl)-3-methyl-2-butenyl]-7-(3-methyl-2-butenyl)-indole (3)

Chromatography of fraction P_6 (2 x 110 mg) on PVA 500 (15 g each, methanol) afforded 3 (38 mg), which was crystallized from petroleum ether/ethyl acetate to give colorless needles, mp 106-108°C; $[\alpha]_D^{20}$= ±0° (c = 1.0). TLC: Rf = 0.23, anisaldehyde: orange-red; UV: λ_{max}(log ε) = 221 (4.85), 280 (4.20), 289 nm (sh 4.12); MS: m/z (rel. int.) = 368.2253 (98%, M^+; $C_{26}H_{28}N_2$), 353 (21), 184 (29), 168 (100); ^{1}H-NMR: δ = 8.00 (br s; 1H, NH), 7.95 (br s; 1H, NH), 7.53 (d, J = 7.8 Hz; 1H, 4"-H), 7.29 (d, J = 7.3 Hz; 1H, 4-H), 7.13 (d, J = 7.2 Hz; 1H, 6"-H), 7.07 (t, J = 7.5 Hz; 1H, 5"-H), 7.02 (dd, J_1= 3.2 Hz, J_2= 2.4 Hz; 1H, 2"-H), 6.99 - 6.94 (m; 2H, 5-H and 6-H); 6.83 (dd, J_1= 2.4 Hz, J_2= 1 Hz; 1H, 2-H), 6.49 (dd, J_1= 3.2 Hz, J_2= 2.2 Hz; 1H, 3"-H), 5.76 (dqq, J_1= 9.3 Hz, J_2= J_3= 1.4 Hz; 1H, =CH-CH), 5.41 (tqq, J_1= 7.1 Hz, J_2= J_3= 1.4 Hz; 1H, =CH-CH_2), 5.38 (d, J = 9.3 Hz; 1H, =CH-CH), 3.55 (d, J = 7.1 Hz; 2H, =CH-CH_2), 1.82 and 1.80 (2 x s; 9H, =C-CH_3), 1.77 (s; 3H, =C-CH_3); ^{13}C-NMR: δ = 136.0 (s; C-7a), 134.7 (s; C-7a"), 133.2 (s; C-3'), 132.4 (s; C-3"), 128.2, 127.1 and 126.9 (3 x s; C-7", C-3a, C-3a"), 126.5 (d; C-2"), 124.0 (s; C-7), 123.6 (d; C-2"), 122.1 (d; C-2'), 121.8, 121.7, 121.0, 119.9, 119.7 and 118.9 (6 x d), 118.9 (s; C-3), 117.7 (d), 102.5 (d; C-3"), 38.9 (d; C-1"), 30.6 (t; C-1'), 25.7 (q; C-4' and C-4"), 18.1 and 17.9 (2 x q; C-5', C-5").

Annonidine B = 3-[1-(3-Indolyl)-3-methyl-2-butenyl]-7-(3-methyl-2-butenyl)-indole (4)

Chromatography of fraction P_{10} (2 x 67 mg) on PVA 500 (15 g each, methanol) yielded 4 (11 mg). TLC: Rf = 0.13, anisaldehyde: yellow-orange; UV: λ_{max}(log ε) = 226 (4.83), 283 (4.13), 291 nm (sh 4.08); MS: m/z (rel. int.) = 368 (100%, M^+), 353 (47), 313 (18), 168 (15); ^{1}H-NMR: δ = 7.86 (br s; 1H, NH), 7.83 (br s; 1H, NH), 7.53 (d, J = 7.6 Hz; 1H, 4"-H), 7.40 (m; 1H, 4-H), 7.32 (d, J = 8.3 Hz; 1H, 7"-H), 7.15 (m; 1H, 6"-H or 5"-H), 7.03 (m; 1H, 5"-H or 6"-H), 6.97 (m; 2H, 5-H and 6-H), 6.88 and 6.86 (2 x dd, J_1= 2.2 Hz, J_2= 0.8 Hz; 2H, 2-H and 2"-H), 5.71 (dqq, J_1= 9.5 Hz, J_2= J_3= 1.5 Hz; 1H, =CH-CH), 5.41 (tqq, J_1= 7.1 Hz, J_2= J_3= 1.5 Hz; 1H, =CH-CH_2), 5.35 (d, J = 9.5 Hz; 1H, =CH-CH), 3.54 (d, J = 7.1 Hz, 2H, =CH-CH_2), 1.86 (d, J = 1.2 Hz; 3H, =C-CH_3), 1.80 (br s; 3H, =C-CH_3), 1.77 and 1.76 (2 x d, J = 1.2 Hz; 6H, =C-CH_3); ^{13}C-NMR: δ = 136.8 and 136.0 (2 x s; C-7a, C-7a"), 133.0 (s; C-3'), 130.6 (s; C-3"), 128.0, 127.1 and 127.0 (2 x s; C-3a,

C-3a"), 123.8 (s; C-7), 122.4 , 121.9, 121.7, 121.6, 121.3, 120.3 and 120.0 (2 x s; C-3, C-3"), 120.0, 119.2, 119.0, 118.0, 111.0 (C-7"), 33.4 (C-1'"); 30.7 (C-1'), 25.7 (C-4' and C-4'"), 18.0 and 17.9 (C-5', C-5'").

Annonidine C = (E)-3-[3-(7-Indolyl)-1,1-dimethyl-2-propenyl]-7-(3-methyl-2-butenyl)-indole (5)

Chromatography of fraction P_8 (2 x 120 mg) on PVA 500 (15 g each, methanol) gave **5** as a colorless oil (54 mg). TLC: Rf = 0.19, anisaldehyde: red; UV: λ_{max}(log ε) = 224 (4.77), 238 (sh 4.51), 292 (4.22), 310 nm (sh 4.13); MS: m/z (rel. int.) = 368.2252 (100%, M^+, $C_{26}H_{28}N_2$), 353 (47), 168 (68); ^{1}H-NMR: δ = 8.16 (br s; 1H, NH), 7.99 (br s; 1H, NH), 7.65 (m; 1H, 4-H), 7.50 (d, J = 7.8 Hz; 1H, 4-H"), 7.19 (d, J = 7.3 Hz; 1H, 6"-H), 7.08 (m; 3H), 6.99 (m; 2H), 6.67 and 6.55 (AB-system, J = 16.4 Hz; 2H, trans - CH=CH), 6.52 (dd, J_1= 3.2 Hz, J_2= 2.2 Hz; 1H, 3"-H), 5.44 (tqq, J_1= 7.1 Hz, J_2= J_3= 1.5 Hz; 1H, =CH-CH_2), 3.58 (d, J = 7.1 Hz; 2H, =CH-CH_2), 1.83 and 1.79 (2 x s; 6H, =C(CH_3)$_2$), 1.66 (s; 6H, >C(CH_3)$_2$); ^{13}C-NMR: δ = 141.4 (d; C-2'"), 136.4 (s; C-7a), 133.7 (s; C-7a"), 133.2 (s; C-3'), 128.3 and 126.1 (2 x s; C-3a, C-3a"), 124.4 and 124.2 (2 x s; C-7, C-3 or C-7"), 123.9 (d), 122.8 (d), 122.2 (d), 122.0 (s; C-7" or C-3), 121.3 (d), 120.0 (3 x d), 119.4 (2 x d), 119.3 (d), 102.9 (d; C-3"), 37.6 (s; C-1'"), 30.7 (t; C-1'), 28.8 (q; C-4'" and C-5'"), 25.6 (q; C-4'), 17.9 (q; C-5').

3-[3-(7-Indolyl)-1,1-dimethylpropyl]-7-(3-methylbutyl)-indole (**8**)

5 (20 mg) was hydrogenated at 20°C on PtO_2 in ethanol. After purification by chromatography on PVA 500 (15 g, methanol) the product (15 mg) formed colorless crystals from petroleum ether, mp 118-119°C.

TLC: Rf = 0.26, anisaldehyde: orange-red; UV: λ_{max}(log ε) = 219 (4.82), 280 (4.10), 288 nm (sh 4.02); MS: m/z (rel. int.) = 372 (21%, M^+), 229 (32), 228 (100), 214 (5), 170 (8), 130 (29); ^{1}H-NMR (90 MHz): δ = 7.95 (br s; 1H, NH), 7.71 (m; 1H, 4-H), 7.40 (m; 1H, 4"-H), 7.33 - 6.83 (m; 6H), 6.71 (dd, J_1= 3.2 Hz, J_2= 2.4 Hz; 1H, 2"-H), 6.38 (dd, J_1= 3.2 Hz, J_2= 2 Hz; 1H, 3"-H), 2.86 (m, 2H), 2.63 - 2.06 (m; 4H), 1.67 (m; 3H), 1.51 (s; 6H, >C(CH_3)$_2$), 1.00 (d, J = 5.6 Hz; 6H, CH(CH_3)$_2$); ^{13}C-NMR: δ = 136.6 (s; C-7a), 134.5 (s; C-7a"), 127.6 and 126.1 (2 x s; C-3a, C-3a"), 125.6 and 125.3 (2 x s; C-7 and C-7"), 124.6 (s; C-3), 123.5, 121.4 (two signals), 121.1, 119.7, 119.5, 118.7, 118.3, 102.4 (C-3"), 42.9 (C-2'"), 38.8 (C-2'), 35.5 (s; C-1'"), 29.0 (C-1'), 28.6 (C-4'" and C-5'"), 28.1 (C-3'), 27.6 (C-3'"), 22.6 (C-4' and C-5').

Annonidine D = (E)-3-[3-(6-Indolyl)-1,1-dimethyl-2-propenyl]- 7-(3-methyl-2-butenyl)-indole (**6**)

Fraction P_{12} mainly consisted of polycarpol (**1**). Chromatography of the methanol-soluble part (65 mg) of this fraction on PVA 500 (15 g, methanol) afforded **1** (40 mg) and **6** (7 mg) as a color-

less oil. TLC: Rf = 0.09, anisaldehyde: red-brown; UV: λ_{max}(log ε) = 225 (4.75), 238 (sh 4.54), 247 (sh 4.49), 292 nm (4.41); MS: m/z (rel. int.) = 368 (100%, M^+), 353 (53), 168 (33); ^{1}H-NMR: δ = 7.95 (br s; 1H, NH), 7.92 (br s; 1H, NH), 7.63 (m; 1H, 4-H), 7.52 (d, J = 8.3 Hz; 1H, 4"-H), 7.23 (br s; 1H, 7"-H), 7.20 (dd, J_1= 8.3 Hz, J_2= 1.5 Hz; 1H, 5"-H), 7.11 (dd, J_1= 3.2 Hz, J_2= 2.4 Hz; 1H, 2"-H), 6.99 (d, J = 2.4 Hz; 1H, 2-H), 6.97 (m; 2H, 5-H and 6-H), 6.53 (AB-system, J = 16.5 Hz; 2H, trans - CH=CH), 6.47 (ddd, J_1= 3.2 Hz, J_2= 2.2 Hz, J_3= 1 Hz; 1H, 3"-H), 5.42 (tqq, J_1= 7.1 Hz, J_2= J_3= 1.5 Hz; 1H, =CH-CH_2), 3.55 (br d, J = 7 Hz; 2H, =CH-CH_2), 1.81 and 1.77 (2 x s; 6H, =C(CH_3)$_2$), 1.62 (s; 6H, >C(CH_3)$_2$); ^{13}C-NMR: δ = 138.3 (C-2'"), 136.4 and 136.3 (2 x s; C-7a, C-7a"), 133.1 (s; C-3'), 132.5 (s; C-6"), 127.0, 127.0, 126.2 and 125.1 (3 x s; C-3a, C-3a", C-3), 124.3, 124.0 (s; C-7), 122.3 (C-2'), 121.2, 120.5, 119.9, 119.6, 119.2, 118.7, 108.8 (C-7"), 102.6 (C-3"), 37.1 (s; C-1'"), 30.7 (C-1'), 28.8 (C-4'" and C-5'"), 25.6 (C-4'), 17.9 (C-5').

3-[3-(6-Indolyl)-1,1-dimethylpropyl]-7-(3-methylbutyl)-indole (**9**)

6 (2 mg) was hydrogenated at 20°C on PtO_2 in ethanol yielding a homogenous product (2 mg). TLC: Rf = 0.14, anisaldehyde: orange-red; UV: λ_{max}(log ε) = 221 (4.82), 281 (4.10), 291 nm (4.05); MS: m/z (rel. int.) = 372 (32%, M^+), 229 (54), 228 (100), 214 (6), 170 (5), 130 (22); ^{1}H-NMR (90 MHz): δ = 7.88 (br s; 2H, 2 x NH), 7.70 (m; 1H, 4-H), 7.48 (d, J = 8 Hz; 1H, 4"-H), 7.15 - 6.94 (m; 6H), 6.85 (dd, J_1= 8 Hz, J_2= 1.5 Hz; 1H, 5"-H), 6.46 (m; 1H, 3"-H), 2.82 (m; 2H), 2.62 - 2.06 (m; 4H), 1.66 (m; 3H), 1.50 (s; 6H, >C(CH_3)$_2$), 1.00 (d, J = 5.6 Hz; 6H, CH(CH_3)$_2$).

Annonidine E = (E)-3-[3-(7-Indolyl)-1,1-dimethyl-2-propenyl]-7-(3-methyl-2,3-epoxybutyl)-indole (**7**)

Fraction P_{14} was separated on PVA 500 (15 g, methanol). The fraction containing **7** was rechromatographed on the same column to give pure **7** (2 mg). TLC: Rf = 0.07, anisaldehyde: red; UV: λ_{max}(log ε) = 224 (4.83), 238 (sh 4.53), 293 (4.27), 310 nm (sh 4.16); MS: m/z (rel. int.) = 384 (100%, M^+), 369 (49), 313 (7), 297 (21), 182 (10), 168 (49), 167 (15), 130 (16); ^{1}H-NMR: δ = 9.07 (br s; 1H, NH), 8.19 (br s; 1H, NH), 7.69 (m; 1H, 4-H), 7.50 (d, J = 7.8 Hz; 1H, 4"-H), 7.20 (d, J = 7.3 Hz; 1H, 6"-H), 7.11 (m; 2H, 2-H and 2"-H), 7.07 (t, J = 7.6 Hz; 1H, 5"-H), 6.97 (m; 2H, 5-H and 6-H), 6.67 and 6.56 (AB-system, J = 16.2 Hz; 2H, trans - CH=CH), 6.52 (dd, J_1= 3.2 Hz, J_2= 2.0 Hz; 1H, 3"-H), 3.24 (dd, J_1= 14.8 Hz, J_2= 1.5 Hz; 1H, ^{O}>CH-CH_2), 3.05 (dd, J_1= 9.3 Hz, J_2= 1.5 Hz; 1H) and 2.96 (dd, J_1= 14.8 Hz, J_2= 9.3 Hz; 1H, ^{O}>CH-CH_2), 1.66 (s; 6H, >C(CH_3)$_2$), 1.52 and 1.39 (2 x s; 6H, ^{O}>C(CH_3)$_2$); ^{13}C-NMR: δ = 141.6 (C-2'"), 136.8 (s; C-7a), 133.7 (s; C-7a"), 128.2 and 126.3 (2 x s; C-3a, C-3a"), 123.9 (s; C-3 or C-7"), 123.9, 122.8, 122.0, 122.0 and 121.8 (2 x s; C-7, C-7" or C-3), 120.7, 120.2, 120.1, 119.9, 119.4, 118.9, 102.9 (C-3"), 64.5 (C-2'), 59.8 (s; C-3'), 37.5 (s; C-1'"), 33.5 (C-1'), 28.9 (C-4'" and C-5'"), 24.7 (C-4'), 18.9 (C-5').

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