Pergamon

Tetrahedron, Vol. 53, No. 47, pp. 16177-16184, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)10076-X

The Acylation-Dimerization of Precocene II

Braulio M. Fraga,* Inmaculada Cabrera,† Victor P. García, Ricardo Guillermo† and Aurea Perales‡

Instituto de Productos Naturales y Agrobiología, CSIC, P.O. Box 195, La Laguna, 38206-Tenerife, Spain

† Departamento de Química Orgánica, Universidad de La Laguna, Tenerife

‡ Departamento de Rayos X, Instituto Rocasolano, CSIC, Serrano 117, 28006-Madrid, Spain

Abstract: Ferric trichloride in acetic anhydride has been used in the acylation and dimerization-acylation of precocene II. The acylation of this antijuvenile hormone occurs in the chromene ring and not in the aromatic one, whilst in the dimers obtained one of the benzenic rings was acylated. In this reaction the first trimer of precocene II has also been obtained. The same reaction was studied using $ZnBr_2$ as Lewis acid. © 1997 Elsevier Science Ltd.

In previous works we have studied the dimerization of the antijuvenile hormone precocene II (**1**) with different Lewis acids supported on silica gel.[1] Later, the 3,3'-dimer of precocene II was obtained by reaction of **1** with ferric trichloride in acetic acid.[2] Continuing with these works, we describe here the results obtained from the reaction of **1** with ferric trichloride/Ac_2O and with zinc bromide/Ac_2O.

Ether cleavage with ferric chloride/acetic anhydride has been reported.[3] On the other hand, ferric chloride in silica gel has been used in the dehydration of alcohols,[4,5] in the cleavage of acetals and ketals[6] and in the coupling of phenol ethers.[7]

In this work we showed that the reaction of precocene II (**1**) with $FeCl_3$ in Ac_2O led to the acylated precocene II **3**, the dimer **5**, the monoacylated dimers **6** and **7**, the diacylated dimer **8**, the symmetrical dimer **9**. and the trimer **10**. Compound **5** was identical with that obtained by treatment of precocene II with mineral acids,[8] and it is derived from the reaction of the benzylic carbocation ion **4**, formed in the complexation of precocene II (**1**) with the Lewis acid, with a second molecule of **1** (Scheme 1).

Compound **3** was a monomeric substance shown to contain an acetyl group. The molecular ion in the MS spectrum was in accordance with the formula $C_{14}H_{18}O_4$. Comparing its ^1H NMR spectrum with that of precocene II (**1**) it was clear that one of the vinylic hydrogens of the chromene ring had been substituted by the

acetyl group. The exact position C-3 was deduced from its ^{13}C NMR spectrum (Table 1), which was assigned using COSY, HMQC and HMBC NMR spectra. Thus, in the last experiment, correlations can be observed between the methyl hydrogens (H-11 and H-12) with two quaternary centres, C-2 and C-3.

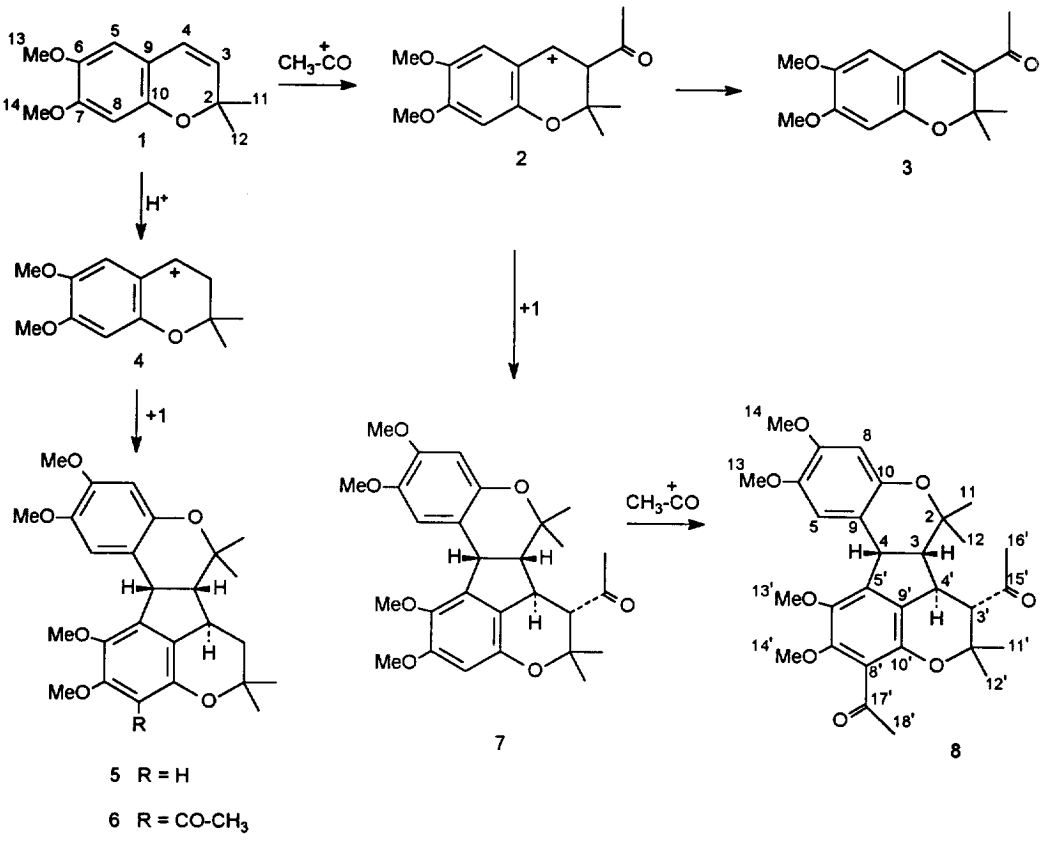
The structure of the dimer **6** was given on the basis of the following consideration: The molecular ion appears in its high-resolution MS at m/z 482.2278, which was in accordance with the formula $C_{28}H_{34}O_7$. Other main fragments observed in this spectrum were those formed from the molecular ion by the loss of a methyl, methoxy and acetyl group, at m/z 467, 451 and 440, respectively. Its ^1H NMR spectrum showed four methyl and four methoxy groups, indicating that at least two molecules of **1**, formed part of its structure. The other two carbons were derived from an acetic anhydride molecule and corresponded to a $-CO-CH_3$ group with proton resonance at δ 2.49 (s). The remainder of the signals were similar to those described for compound **5**,[8] although only two aromatic hydrogens appear in **6**. This indicated that in **5** an aromatic proton has been replaced by an acetyl group to form **6**. On the other hand, the introduction in the molecule of this group does not affect the chemical shifts of the two aromatic hydrogens, compared with those of **5**, indicating that the acetyl group is at C-8', a position sufficiently distant from H-5 and H-8. This assertion was confirmed by ^{13}C NMR studies. Thus using 2D NMR experiments, HMQC and HMBC with gradient, we can assign unequivocally the carbon resonances of precocene II (**1**), the acylated precocene **3** and all the dimers described in this work (see Table 1). Previously, only some selected carbons of precocene II derivatives had been assigned.[9]

We also obtained **6** by direct acylation of the dimer **5** with the same reagent $FeCl_3/Ac_2O$ under the same conditions as those under which **1** was treated. Thus, in the reaction the dimer **5** must first be formed, and then acylated at C-8' to give **6**.

Another acylated dimer was obtained in this reaction and assigned the structure **7**. Its molecular formula, determined by HRMS, was $C_{28}H_{34}O_7$, which indicated that this compound was isomeric with **6**. Its ^1H NMR spectrum showed the methyl of an acylated function at δ 2.33 and three aromatic hydrogens, indicating that the acetyl group was in the non-aromatic part of the molecule. A comparison with the corresponding spectrum of **6** permitted the assignment of its ^1H NMR spectrum. Thus, in **7** H-4 appears at δ 4.45 (d, J = 7 Hz), H-3 at δ 2.36 (dd, J = 10 and 7 Hz), H-4' at 3.38 (t, J = 10 Hz) and H-3' at δ 2.68 (d, J = 10 Hz). The number and the form of resonances of the hydrogens at C-3' and C-4' indicated that the acetyl group was located at C-3'. Its equatorial α-stereochemistry was deduced from the observed coupling constant (J = 10 Hz) between H-3' and H-4', which indicated a *trans* relationship in 3,4-disubstituted 2,2-dimethyl-dihydro-benzopyrans.[10] The assignment of the ^{13}C NMR spectrum (Table 1), using HMQC and HMBC experiments, confirmed the structure of **7**.

A diacylated dimer of molecular weight m/z 524.2427 and formula $C_{30}H_{36}O_8$ was also obtained and assigned structure **8**. Its ^1H NMR spectrum showed the resonance of the methyls of two acylated functions at

δ 2.33 and 2.45. The resonances of H-4, H-3, H-4' and H-3' were very similar to those of **7**, while that those of the aromatic protons, H-5 and H-8, and methoxy groups were analogous to those of **6**, which indicated that the acylated positions should be C-3' and C-8'. Indeed, the stereochemistry at C-3' was the same as in **7**. 2D NMR studies confirmed the structure and permitted the assignment of the carbon resonances (Table 1).



Scheme 1

The mechanism of formation of these compounds can be explained as a Friedel-Crafts acylation, by the acetyl cation (Scheme 1). Although the type of aromatic acylation that afforded **6** is well-known, this is the first time that it has been reported to occur on a chromene double bond, as in **3**. The acylation in this position may be influenced by the presence of the methoxy group at C-7, which would stabilize a benzylic carbocation at C-4. In the formation of compound **6**, we think that the preference for acylation at C-8', rather than at C-5 or C-8, is due to the fact that the C-5' position is alkylated, favouring the *para*-acylation at C-8'.

The formation of the monoacylated dimer 7 implies the reaction of a molecule of precocene II (**1**) with the acylated precocene II (**3**), as described in the scheme. The dimer 7 can then also be acylated at C-8' to give the diacylated dimer **8**.

We attempted to confirm the structure of one of the acylated dimers **6-8** by X-ray analysis but suitable crystals were not available. However, we could resolve by this method the structure of the intermediate dimer **5**, confirming the structure and stereochemistry previously given by Kasturi et al.[3] This last dimer had been obtained by treatment of **1** with acetic acid-sulfuric acid.

Fig.1 shows a perspective of the molecule of **5** viewed down the b-axis, with the numbering of the atoms. The central carbon skeleton comprises a five rings system: two benzene rings, two dihydropyran rings and one five-membered ring. The C/D fusion is *cis* with both H-atoms, H-3 and H-4, in ß-configuration. The angle between rings D and C is 109.81°. Ring B has an envelope conformation and ring D has a half-chair form. The fusion of the rings E/D is nearly planar, the angle between them being 1.6°, while the angle between A/B is greater, 14.5°. The molecule is not planar, but it shows a bending between these two more planar ends (rings A/B and rings E/D).

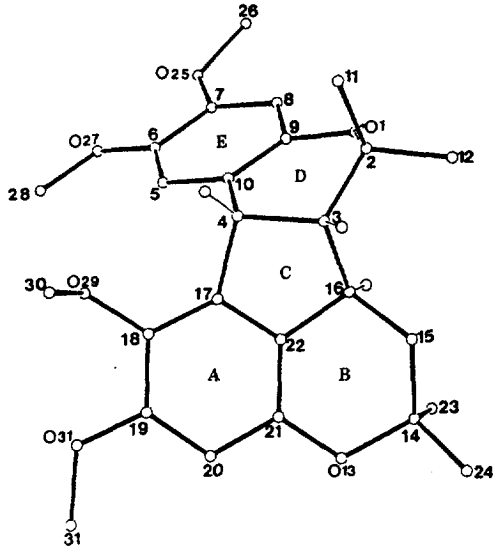


Fig 1. Perspective drawing of **5** with the atomic-numbering scheme used in X-ray analysis.

The symmetrical dimer **9** was also obtained in this reaction. This compound was identical with one formed in the reaction of precocene II (**1**) with ferric trichloride/acetic acid, and occurs by oxidative one-electron coupling reactions.[2]

Table 1. ^{13}C NMR Data[#]

C	1	3	5	6	7	8	9
2	75.9	79.7	75.6	75.8	74.8	74.8	78.9
3	128.1	136.0	58.1	57.8	58.2	57.9	135.7
4	121.9	133.7	41.1	41.4	41.9	42.1	122.7
5	109.7	110.6	112.9	112.6	112.0	111.9	110.5
6	143.0	143.7	143.8	144.0	143.4	143.5	143.7
7	149.6	152.9	148.6	148.9	148.4	148.6	150.2
8	101.0	100.7	101.3	101.4	100.9	101.1	101.3
9	113.0	111.7	113.7	113.3	113.0	112.5	114.5
10	147.6	149.5	145.9	145.5	145.9	144.4	146.9
11	27.6	26.3	25.6[a]	25.8[a]	28.1	28.0[a]	27.0
12	27.6	26.3	28.3[a]	28.5[a]	28.2	28.8[a]	27.0
13	55.8	55.9	55.8	56.1	55.7	55.7	56.1
14	56.5	56.4	56.3	56.3	56.2	55.9	56.7
15	---	195.9	---	---	---	---	---
16	---	26.5	---	---	---	---	---
2'	---	---	76.8	77.8	77.7	78.4	78.9
3'	---	---	41.4	41.1	60.3	58.9	135.7
4'	---	---	34.2	34.8	38.5	38.8	122.7
5'	---	---	136.9	139.0	137.0	139.0	110.5
6'	---	---	138.6	142.2	138.4	142.0	143.7
7'	---	---	153.4	150.6	153.4	150.3	150.2
8'	---	---	99.0	n.o.	98.7	n.o	101.3
9'	---	---	118.8	123.3	118.6	123.0	146.9
10'	---	---	148.3	145.5	147.5	146.0	114.5
11'	---	---	25.9[b]	26.3[b]	21.1[b]	21.6[b]	27.0
12'	---	---	30.1[b]	30.2[b]	26.0[b]	26.5[b]	27.0
13'	---	---	60.7	61.1	60.8	60.8	56.1
14'	---	---	56.1	61.9	56.1	61.4	56.7
15'	---	---	---	201.2	---	200.5	---
16'	---	---	---	30.7	---	32.4	---
17'	---	---	---	---	211.4	211.0	---
18'	---	---	---	---	35.2	35.1	---

[#]The data of the trimer **10** are given in the experimental part.

[a,b] These values can be interchanged

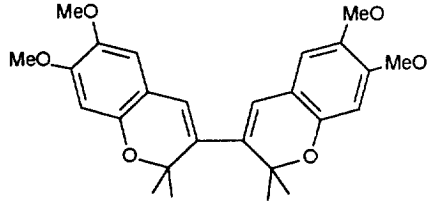
n.o. Not observed

Finally, the structure **10** was assigned to a trimer obtained in the reaction of precocene II with $FeCl_3/Ac_2O$ in very low yield. Its high resolution MS was in accordance with the molecular formula $C_{39}H_{48}O_9$, indicating that it is formed by three molecules of **1**. Thus, the ^1H NMR spectrum showed six methyl and six methoxyl groups and six aromatic protons. Other signals observed in the spectrum were two double doublets at δ 2.48 (J = 16 and 4 Hz) and 2.72 (J = 16 and 8 Hz), assigned to the two H-4 atoms, a broad signal at δ 2.01 ($W_{1/2}$ = 14 Hz) due to H-3, two broad doublets centred at δ 3.14 and 3.32, with a

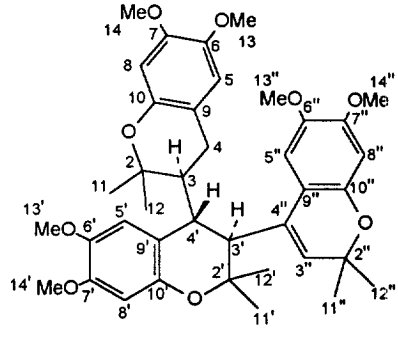
coupling constant of 9 Hz, corresponding to H-3' and H-4', respectively, and a singlet at δ 5.35 assigned to H-3". Double resonance experiments and COSY spectrum confirmed the couplings and the assignments. ^{13}C NMR spectrum (see experimental) and 2D NMR spectra, HMQC and HMBC, confirmed the structure assigned. For example, the signal of H-3" showed correlations with C-11", C-12", C-2", C-9" and C-3', while the H-3' signal presented correlations with C-2', C-4', C-9' and C-3. Moreover, the signal of H-4' showed correlations with C-3, C-2', C-3', C-5' and C-9', while one of H-4 (δ 2.70, α-axial) gave correlations with C-3, C-5 and C-4'. The stereochemistry of **10** was given considering the coupling constants observed in the ^1H NMR spectrum. The formation of this trimer, in very low yield, occurs via the less stable carbonium ion at C-3, whilst that of the dimer **5**, takes place *via* the more stable C-4 ion.

Zinc bromide was examined as an alternative Lewis acid in this acylation-dimerization reaction. When precocene II (**1**) in acetic anhydride was treated with zinc bromide, compound **3** was obtained in good yield, while dimers **6-8** were also formed as minor products. As expected for a reagent which is not a one-electron transfer oxidant, dimer **9** was not formed. Thus, this is the reagent to choose when the acylation of precocene II and related compounds in the pyran ring is required.

In summary, the acylation of precocene II opens up the way to the preparation of new derivatives of this antijuvenile hormone and of other chromenes with an activated double bond, such as lapachenole[3,11] and N-methylflindersine.[12]



9



10

EXPERIMENTAL

Reaction of Precocene II with Iron(III) Chloride-Acetic Anhydride. To a solution of precocene II (**1**) (200 mg) in acetic anhydride (1 ml), iron (III) chloride (100 mg) was added and kept with stirring, under nitrogen, for 1 h at room temperature. Usual work-up and chromatography of the residue, eluting with petrol-EtOAc (8:2), afforded **3** (40 mg), **5** (9 mg), **6** (60 mg), 7 (8 mg), **8** (4 mg), **9** (50 mg).and **10** (3 mg)

Acylated precocene II (**3**). M.p. 123-125°; $[M]^+$ at *m/z* 262.1203. $C_{15}H_{18}O_4$ requires 262.1205; IR ($CHCl_3$) υ_{max} cm^{-1}: 3015, 1660, 1614, 1567, 1507, 1465, 1367, 1147; ^1H NMR (200 MHz): δ 1.56 (6H, s), 2.38 (3H, s, CH_3-CO), 3.84 and 3.86 (each 3H, s, -OMe), 6.41 (1H, s), 6.63 (1H, s), 7.18 (3H, s); UV λ_{max} nm 307 and 257; ^1H NMR (C_6D_6, 200 MHz): δ 1.91 (6H, s), 2.07 (3H, s, CH_3-CO), 3.25 and 3.35 (each 3H,

s, -OMe), 6.36 (1H, s), 6.38 (1H, s), 6.74 (1H, s); EIMS *m/z* (rel. int.): 262 $[M]^+$ (23), 247 (100), 219 (16), 203 (8),189 (4), 175 (6), 115 (5), 91 (7).

Dimer (**5**). ^1H NMR (500 MHz): δ 1.25 and 1.40 (each 3H, s, H-11' and H-12'), 1.34 and 1.47 (each 3H, s, H-11 and H-12), 1.38 (1H, overlapped signal, H-3'), 2.14 (1H, dd, J = 13 and 5 Hz, H-3'), 2.24 (1H, dd, J = 10 and 7.5 Hz, H-3), 3.12 (1H, ddd, J = 12, 10 and 5 Hz, H-4'), 3.76 (3H, s, H-13), 3.77 (3H, s, H-14), 3.79 (3H, s, H-14'), 3.90 (3H, s, H-13'), 4.41 (1H, d, J = 7.5 Hz, H-4), 6.21 (1H, s, H-8'), 6.34 (1H, s, H-8), 7.28 (1H, s, H-5).

8'-Acylated dimer (**6**). M.p. 181-183°, $[M]^+$ at *m/z* 482.2278. $C_{28}H_{34}O_7$ requires 482.2302; ^1H NMR (500 MHz): δ 1.26, 1.37, 1.41 and 1.50 (each 3H, s), 1.43 (1H, overlapped signal, H-3'), 2.17 (1H, dd, J = 13 and 5 Hz, H-3'), 2.30 (1H, dd, J = 10 and 7.5 Hz, H-3), 2.49 (3H, s, H-18'), 3.14 (1H, ddd, J = 12, 10 and 5 Hz, H-4'), 3.77, 3.80, 3.84 and 3.96 (each 3H, s), 4.43 (1H, d, J = 7.5 Hz, H-4), 6.40 (1H, s, H-8), 7.26 (1H, s, H-5); EIMS *m/z* (rel. int.): 482 $[M]^+$ (100), 467 (9), 451 (30), 439 (6), 427 (25), 411 (33), 273 (20), 233 (17), 195 (42), 167 (28).

3'-Acylated dimer (**7**). $[M]^+$ at *m/z* 482.2273. $C_{28}H_{34}O_7$ requires 482.2304; ^1H NMR (500 MHz): δ 1.31, 1.33, 1.34 and 1.36 (each 3H, s), 2.33 (3H, H-16'), 2.36 (1H, dd, H-3, J = 7 and 10 Hz, H-3), 2.68 (1H, d, J = 10 Hz, H-3'), 3.38 (1H, t, J = 10 Hz, H-4'), 4.45 (1H, d, J = 7 Hz, H-4), 6.22 (1H, s, H-8'), 6.32 (1H, s, H-8), 7.24 (1H, s, H-5); EIMS *m/z* (rel. int.): 482 $[M]^+$ (100), 467 (15), 451 (25), 439 (11), 385 (10), 369 (9), 353 (11), 307 (6), 195 (19), 167 (20), 149 (18).

Diacylated dimer (**8**). M.p. 234-235°, $[M]^+$ at *m/z* 524.2427. $C_{30}H_{36}O_8$ requires 524.2410; mp 234-235; ^1H NMR (500 MHz): δ 1.29, 1.30, 1.32 and 1.34 (each 3H, s), 2.33 (3H, s, H-16'), 2.39 (1H, dd, J = 10 and 8 Hz, H-3), 2.45 (3H, s, H-18'), 2.73 (1H, d, J = 10 Hz, H-3'), 3.39 (1H, t, 10 Hz, H-4'), 3.74, 3.78, 3.84 and 3.94 (each 3H, s), 4.45 (1H, d, J = 8 Hz, H-4), 6.35 (1H, s, H-8), 7.19 (1H, s, H-8); EIMS *m/z* (rel. int.): 524 $[M]^+$ (100), 509 (5), 493 (28), 481 (60), 467 (8), 451 (6), 439 (7), 427 (10), 411 (29), 395 (16), 327 (7), 273 (5), 205 (6), 195 (18), 167 (18).

Symmetrical dimer (**9**). ^1H NMR (200 MHz): δ 1.52 (12 H, s), 3.83 and 3.85 (each 6H, s), 6.19 (2H, s, H-4 and H-4'), 6.45 (2H, s, H-8 and H-8'), 6.55 (2H, s, H-5 and H-5'); EIMS *m/z* (rel. int.): 438 $[M]^+$ (7), 423 (100), 219 (8), 204 (35), 196 (7).

Trimer (**10**). $[M]^+$ at *m/z* 661.3319. $C_{39}H_{48}O_9$ requires 660, 3298; ^1H NMR (500 MHz): δ 1.16, 1.22, 1.25, 1.36, 1.40 and 1.52 (each 3H, s), 2.01 (1H, br signal, $W_{1/2}$ = 14 Hz, H-3), 2.48 (1H, dd, J = 16 and 4 Hz, H-4), 2.72 (1H, dd, J = 16 and 8 Hz, H-4), 3.14 and 3.32 (each 1H, br d, J = 9 Hz, H-3' and H-4'), 3.57, 3.68, 3.74, 3.75, 3.83 and 3.84 (each 3H, s), 5.35 (1H, s, H-3"), 6.27 (2H, s), 6.31, 6.37 and 6.44 (each 1H, s), 6.85 and 6.87 (each 1H, s); ^{13}C NMR (125 MHz), quartets: δ 21.5 and 26.9 (C-11' and C-12'), 26.1 and δ 28.8 (C-11 and C-12), 27.5 and 28.5 (C-11" and C-12"), 55.6, 55.7, 55.8, 56.0, 56.2 and 57.0 (6 -OMe), triplet: 24.2 (C-4), doublets: 40.7 (C-4'), 43.6 (C-3), 47.6 (C-3'), 101.2, 101.4 and 101.6 (C-8, C-8' and C-8"), 107.4 (C-5"), 111.9 (C-5'), 113.4 (C-5) and 126.3 (C-3"), singlets: 75.4 (C-2'), 76.4 (C-2'), 77.3 (C-2), 112.2 (C-9 and C-9'), 115 (C-9"), 133.0 (C-4"), 142.5, 143.0 and 143.1 (C-6, C-6' and C-6"), 146.6, 147.5, 148.0, 148.2, 148.3 and 150.0 (C-8, C-8', C-8", C-10, C-10' and C-10"); EIMS *m/z* (rel. int.): 660 $[M]^+$ (35), 645 (5), 439 (20), 423 (11), 274 (7), 259 (85), 221 (9), 220 (16), 219 (8), 205 (80), 167 (25), 149 (92), 57 (100).

Reaction of dimer **5** *with Iron(III) Chloride-Acetic Anhydride.* Compound **5** (45 mg) was treated under the same conditions as precocene II (**1**) (see above) giving the 8'-acylated dimer **6** (32 mg).

Reaction of Precocene II with Zinc (II) Bromide-Acetic Anhydride. To a solution of precocene II (**1**) (200 mg) in acetic anhydride (1 ml), zinc (II) bromide anhydrous (400 mg) was added and kept with stirring, under nitrogen, for 75 min. at room temperature. Usual work-up and chromatography of the residue, eluting

with petrol-EtOAc (8:2), afforded **3** (130 mg), **5** (4 mg), **6** (27 mg), 7 (6 mg) and **8** (5 mg).

Crystallographic Data for the Dimer **5**. Transparent colourless needles, $C_{28}H_{32}O_6$, MW 464.557, crystallized in the monoclinic system, space group $P2_1/n$. The cell dimensions were determined from least-squares analysis of 22 reflections ($\theta<45°$), with a = 16.982(1) Å, b = 11.055(1) Å, c = 12.749(1) Å, ß = 93.970(5)°, Z = 4, F(000) = 992, Dc = 1.302 g cm^{-3} and μ = 7.077 cm^{-1}.

The intensities of 4190 independent Friedel pairs to θ = 65° were alternatively collected on an automatic four-circle Philips PW 1100 diffractometer with graphite monochromated CuKα radiation ($\omega/2\theta$ scan technique, 1.50 scan width). The intensities were corrected by Lorenz and polarization effects, and 1760 Friedel pairs were considered as observed, when $I > 2\sigma(I)$, and used for the structure determination and refinement. Two reference reflections were measured every 90 min. during the data collection process in order to check crystal alignment and/or decomposition. The intensities showed no variation and no crystal decay. The structure was solved by direct methods, and refined by least-squares methods. An empirical weighting scheme was used to give no trends in $<\omega\Delta^2F>$ over ranges of <Fo> and <sin θ/λ>. The final R and Rw values were 0.075 and 0.073, respectively. All calculations were performed on a Vax 11/750 and with MULTAN 86 and X-ray 76 programs.[13,14] Scattering factors were taken from ref.[15] Lists of atomic coordinates, thermal parameters, structure factors, bond lengths, bond angles and torsion angles are deposited as supplementary material.

REFERENCES

1. Fraga, B.M.; García, V.P.; González, A.G.; Hernández, M.G.; Hanson, J.R.;. Hitchcock, P.B *J. Chem. Soc., Perkin Trans. 1* **1983**, 2687-2693.
2. Fraga, B.M.; García, V.P. *J. Org. Chem.* **1987**, 52, 5032-5034.
3. Kasturi, T.R.; Abraham, E.M. Brown, P. *J. Chem. Soc., Perkin Trans.* **1973**, 2468-2470.
4. Ganem B.; Smale, V.R. *J. Org. Chem.* **1974**, 39, 3728-3730.
5. Keinan, E.; Mazur, Y. *J. Org. Chem.* **1978**, 43, 1020-1022.
6. Tal, D.M.; Keinan, E.; Mazur, Y. *Tetrahedron* **1981**, 37, 4327-4330.
7. Kim, K.S.; Song, Y.H.; Lee, B.H.; Hanhn, C.S. *J. Org. Chem.* **1986**, 51, 404-407.
8. Jempty, T.C.; Miller, L.L.; Mazur ,Y. *J. Org. Chem.* **1980**, 45, 749-751.
9. Ottridge, A.P.; Jenning, R.C.; Brook, G.T. in *Juvenile Hormone Biochemistry*; G.E. Pratt and G.T. Brooks, Eds.; Elsevier-North Holland, Amsterdam, 1981; pp. 381-386.
10. Aizawa, H.; Bowers, W.S.; Soderlund, D.M. *J. Agric. Food Chem.* **1985**, 33, 406-411.
11. Livingstone, R.; Whiting, M.C. *J. Chem. Soc.* **1955**, 3631-3636.
12. Grundon, M.F.; Rutherford, M.J. *J. Chem. Soc., Perkin Trans 1* **1985**, 197-198.
13. Main, P.; Fiski, S.J.; Hull, S.E.; Lessinger, L.; Germain, G.; Declecq, J.; Woolfson, M.M. *MULTAN 80*, University of York, U.K., 1980.
14. Stewart, J.M.; Machin, P.A.; Dickinson, D.W.; Ammon, H.L.; Heck, H.; Flack, H.Y. *The X-Ray 76 System*, Tech. Rep. TR. 446, Computer Science Center, University of Maryland, College Park, Maryland, U.S.A., 1976.
15. *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, U.K., 1974.

(*Received in UK* 1 *July* 1997; *revised* 12 *September* 1997; *accepted* 18 *September* 1997)