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ISOPENTENYLATED XANTHONES FROM *KIELMEYERA* AND *CALOPHYLLUM* SPECIES

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Abstract—Isopentenylated xanthones from Brazilian *Kielmeyera* and *Calophyllum* species include, besides the known jacareubin (Ia) and osajaxanthone (Ib), the hitherto undescribed 6-dehydroxyjacareubin (Ic), guanandin (IIa), isoguanandin (III) and dehydrocycloguanandin (XII).

THE chemical constitution of the trunk wood of several Brazilian Guttiferae species has been reported. Besides common triterpenoids and, in two cases, the uncommon aucuparin,[3,4] xanthones were found to be the predominant constituents. Most of these are simple oxygenated derivatives,[3–11] while others are isopentenylated compounds. The present paper is concerned with the identification or structure elucidation of the latter.

Osajaxanthone from Kielmeyera corymbosa.[12] Examination of *K. corymbosa* (Spr.) Mart. produced a minor constituent whose UV spectrum showed, besides the usual bands associated with the xanthone skeleton, an intense absorption at 286 mμ (ε, 47,100). A spectrum of this type has been obtained previously for another constituent of a Guttiferae species, namely jacareubin (Ia).[13–15] The skeleton of a 2,2-dimethylchromenoxanthone which, consequently, may be formulated, must be substituted by two hydroxyls, in view of the mol wt, 310. One of these hydroxyls is located at C-1, since the addition of $AlCl_3$ produced a bathochromic shift of maxima of the original UV spectrum. The second hydroxyl cannot be placed at positions 2 or 4 where it would form part of an *ortho* or a *para* quinol, since the substance is stable in alkali. Presence of a hydroxyl at positions 3, 4, 5 and 6 imparts sufficient acidity to a xanthone to be ionized by sodium acetate. The spectrum of the compound, however, was not altered upon addition of this reagent. Finally, the hydroxyl must also be absent from position 8, since the IR spectrum does not include absorption peaks indicative of 3 vicinal aromatic protons. Only a 1,7-dihydroxy system is thus compatible with the UV and IR data.

All the described structural requirements are embodied in osajaxanthone (Ib), a constituent of the osage orange (*Maclura pomifera* Raf., family Moraceae).[16,*]

6-Dehydroxyjacareubin from Kielmeyera speciosa[17] *and* Calophyllum brasiliense.[18] Jacareubin (Ia) was originally isolated from *Calophyllum brasiliense* Camb.,[13] a timber known by the trivial names of jacareúba or guanandi. A re-investigation of

* Dr. M. L. Wolfrom has kindly informed us that X-ray diffraction data show the identity of his-osajaxanthone with our constituent of *K. corymbosa*.

the extractives of its trunk wood led to the recognition that jacareubin was accompanied by a series of compounds. One of them (for others see Ref. 11 and below), an isomer of osajaxanthone (Ib), was found to occur also in *Kielmeyera speciosa* St. Hil.

The UV spectral data of this compound were comparable to those given by osajaxanthone, with one exception. A bathochromic shift of the maxima was observed upon addition of sodium acetate. The structures differ, consequently, at least with relation to the position of the 7-hydroxyl of osajaxanthone (Ib). While the minute amount of osajaxanthone isolated from *K. corymbosa* had precluded any but UV, IR and mass spectral analysis, sufficient quantity of the new compound was obtained for conclusive NMR examination. As expected, the spectra of the substance and of its methylated derivatives (Table 1) showed the characteristic signals of a 2,2-dimethylchromene group[16] with a singlet due to two methyls and two doublets due to two olefinic protons in a *cis* relationship. Examination of the aromatic region of the spectra revealed a quartet at low field which could be attributed only to a proton at C-8. The chemical shift and coupling constants of this and of other signals showed, on comparison with values obtained for the reference compounds 1,5-dihydroxyxanthone (XIIIa) and 1-hydroxy-5-methoxyxanthone (XIIIb) (Table 1) as well as with calculated values,[19] that the corresponding ring is monosubstituted at C-5. If thus one of the hydroxyls of the original isolate occurs at this position, the other one must be located at C-1, in view of the bathochromic shift of the UV maxima in presence of $AlCl_3$. Indeed, with diazomethane the compound formed only a monomethyl ether. This gave a negative Feigl test[20] and a positive Gibbs test,[14] indicative of the presence of a substituent at C-2 and the absence of a substituent at C-4. The proton at position 4 is represented in the NMR spectra of the isolate and its derivatives by a singlet at relatively high field (Table 1). Clearly, the presence of oxygen functions in the *ortho* and *para* (C-3 and C-1), and not in the *meta* and *para* (C-2 and C-1) relationship is thus indicated.[19]

The data permitted to establish the structure of the isolate as 6-dehydroxyjacareubin (Ic).

Guanandin and isoguanandin from Calophyllum brasiliense.[18] Additional constituents of the jacareúba or guanandí tree include a pair of compounds, guanandin and isoguanandin, mol wt 296. The UV spectra of the isomers were characteristic of simple xanthonic structures, precluding the extension of conjugation of the aromatic system by double bonds. Addition of $AlCl_3$ caused bathochromic shifts of the absorption maxima. Both compounds possess, consequently, a hydroxyl *peri* to the carbonyl group. The second hydroxyl which must exist in view of the mol wt (evidence for an isoprenyl side chain will be presented below) should occur at C-5, since the UV spectra both of guanandin and of isoguanandin resemble the spectrum of 1,5-dihydroxyxanthone. As Table 2 shows, these spectra are distinguished neatly among the spectra of all other dioxygenated 1-hydroxyxanthones.

The NMR spectra of guanandin and of isoguanandin (Table 1) showed some common and some distinctive features. Among the common features, the chemical shifts and splitting patterns of a group of signals, on comparison with values obtained for the reference compounds 1,5-dihydroxyxanthone (XIIIa) and 1-hydroxy-5-methoxyxanthone (XIIIb) as well as with calculated values,[19] clearly placed three protons at positions 2, 3 and 4 of the 1-hydroxylated ring in both substances. In

contradistinction, although in the 5-hydroxylated ring guanandin and isoguanandin sustain two *ortho* protons, the chemical shifts of the respective pairs of doublets show significant differences. The two protons cannot, consequently, be located in identical environment in both substances. Only two possibilities exist for the location of a pair of protons at vicinal positions in 5-hydroxylated xanthone rings. Either they are placed at 7,8, and this must be the case in guanandin in view of the existence of one of the doublets (representing the C-8 proton) at relatively low field, or at 6,7 as, by exclusion, in isoguanandin.

Again, through common spectral features (Table 1), i.e. a singlet due to two olefinic methyl groups, a triplet due to a vinylic proton flanked by a methylene group, the presence of a 3',3'-dimethylallyl side chain lay revealed in both compounds. Only the chemical shifts of the doublet associated with the methylene protons were significantly different in the two spectra. This is not surprising, since the available positions for the side chain are C-6 in guanandin and C-8 in isoguanandin. The expectance that the methylene group in guanandin should be less deshielded than in isoguanandin is fully realized (Table 1).

These facts define guanandin as 1,5-dihydroxy-6-(3',3'-dimethylallyl)xanthone (IIa) and isoguanandin as 1,5-dihydroxy-8-(3',3'-dimethylallyl)xanthone (III), or, more precisely, 4,8-dihydroxy-1-(3',3'-dimethylallyl)xanthone. It should, however, be noted that the argument involved, as important starting point, UV spectral analogies. If these were ignored, NMR would still define inequivocally the 1-hydroxylated ring, but could not distinguish among several additional alternative substitution patterns for the other ring. Thus for guanandin NMR data would be compatible not only with IIa, but also with IVa and, to a lesser degree, with V. For isoguanandin, besides III, VI would also have to be considered.

There was, however, another experimental fact which helped to establish III as the correct structure for isoguanandin, narrowing at the same time the number of hypotheses for guanandin to IIa and IVa. Treatment of isoguanandin with trifluoroacetic acid failed to yield a 2,2-dimethylchromanoxanthone, while, under the same conditions, guanandin was smoothly converted into such a cyclic derivative. The *ortho* relationship of the substituents is thus inacceptable for isoguanandin, while it has to be considered proved for guanandin.

NMR data (Table 1) did not distinguish inequivocally between the two structures VII and VIIIa for cycloguanandin. To choose the correct alternative, guanandin was subjected to treatment with diazomethane. The resulting monomethylether would certainly have either structure IVb, since in IVa steric hindrance would be expected to reduce still further the reactivity of one of the partially chelated hydroxyls; or structure IIb, since it had retained a chelated hydroxyl as shown by shifts of the UV maxima in presence of $AlCl_3$. Failure of this monomethylether to form a chromanoxanthone (VIIIb) confirmed the previous assignment of IIa as the correct structure for guanandin.

Formation of a 2,2-dimethylchroman ring is easily detected through the appearance in the NMR spectrum of two sharp triplets representing two methylene groups at about τ 7 and 8.[21,22] It should not be implied, however, that failure of a compound to cyclize by treatment with acid left its side chain unaltered. In the case of O-methylguanandin, for instance, addition of trifluoroacetic acid to the double bond had occurred (IX), as shown by the presence of a new carbonyl band at 1775 cm^{-1} in

TABLE 1. NMR DATA

Comp.	Aromatic protons at						—CH		$—OCH_3$		$>CH_2$		$>C(CH_3)_2$	—OH	
Solv.	C-2	C-3	C-4	C-6	C-7	C-8									
Inst.	[1]	[1]	[1]	[1]	[1]	[1]	[1]	[1]	[3]	[3]	[2]	[2]	[6]	[1]	[1]
Ic	—	—	3·63	2·61 to 2·85		2·36	3·32	4·29	- -	—	—	—	8·51	−3·24	n.d.
A			s	m		q	d	d					s	s	
100						6·9, 2·8	10·3	10·3							
Id	—	—	3·58	2·67 to 2·87		2·23	3·28	4·43	6·04	—	- -	—	8·53	−3·10	—
C			s	m		q	d	d	s				s	s	
100						6·9, 2·9	10·0	10·0							
Ie	—	—	3·25	2·65 to 2·85		2·14	3·25	4·31	6·01	6·04	—	—	8·52	—	—
C			s	m		q	d	d	s	s			s		
60						6·5, 3·5	10·0	10·0							
IIa	3·23	2·32	2·97	—	2·78	2·33	4·58	- -	—	—	6·45	—	8·23	n.d.	n.d.
A	q	t	q		d	d	t				d		s		
60	8·5, 1·0	8·5	8·5, 1·0		8·5	8·5	7·0				7·0				
IX	3·23	2·44	2·96	—	2·94	2·32	—	—	- -	—	7·08	8·08	8·55	−2·73	—
C	q	t	q		d	d					t	t	s	s	
100	8·0, 1·0	8·0	8·0, 1·0		8·0	8·0					7·0	7·0			
IIb	3·26	2·46	3·06	—	2·86	2·12	4·74	—	6·02	—	6·53	—	8·25	−2·66	—
C	q	t	q		d	d	t		s		d		s	s	
100	8·5, 1·1	8·5	8·5, 1·1		8·5	8·5	7·5				7·5				
XI	3·27	2·48	3·09	—	2·91	2·15	—	—	6·02	—	7·23	7·91	8·39	−2·54	—
C	q	t	q		d	d			s		m	m	s	s	
100	8·3, 1·1	8·3	8·3, 1·1		8·3	8·3									

XII	3·22	2·40	2·98	—	3·00	2·24	3·56	4·17	—	—	—		8·44	n.d.	—
C	q	t	q		d	d	d	d					s		
60	8·3, 1·1	8·3	8·3, 1·1		8·0	8·0	9·8	9·8							
III	3·25	2·33	3·01	2·70	2·90	—	4·58	—		—	6·01	—	8·25	1·14	−2·97
A	q	t	q	d	d		t				d		s	s	s
60	8·3, 1·1	8·3	8·3, 1·1	8·3	8·3		7·0				7·0				
XIIIa	3·22	2·29	2·96	2·61 to 2·80		2·28	—	—	—	—	—	—	—	n.d.	n.d.
A	q	t	q	m		q									
100	8·5, 1·1	8·5	8·5, 1·1			7·4, 2·6									
XIIIb	3·21	2·29	2·95	2·52 to 2·71		2·23	—	—	n.d.	—	—	—	—	n.d.	—
A	q	t	q	m		q									
100	8·5, 1·0	8·5	8·5, 1·0			7·5, 2·1									
XIIIb	3·20	2·40	2·97	2·63 to 2·85		2·16	—	—	n.d.	—	—	—	—	n.d.	—
C	q	t	q	m		q									
100	8·3, 1·0	8·3	8·3, 1·0			6·9, 3·0									

Comp.: For correspondence of numbers with compounds see text and formulae. XIIIa and XIIIb refer, respectively, to 1,5-dihydroxyxanthone and 1-hydroxy-5-methoxyxanthone.

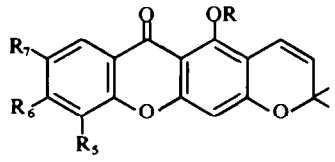
Solv.: A and C means, respectively, use of deuterioacetone and deuteriochloroform as solvent. Tetramethylsilane was used throughout as internal reference.

Inst.: 100 and 60 means, respectively, spectrum taken at 100 Mc/s with a Varian HA-100 NMR Instrument and at 60 Mc/s with a Varian A-60 NMR instrument.

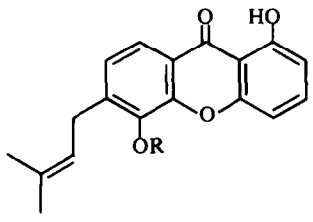
Proton counts: Figures in square brackets indicate proton integrals.

Signals: Each signal is characterized, from top to bottom, by its chemical shift (τ values), splitting pattern (s—singlet, d—doublet, t—triplet, q—quartet, m—multiplet) and coupling constant (c/s); n.d. means signal not determinated.

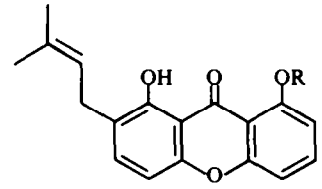
the IR spectrum. The NMR spectrum (Table 1) of the ester IX contains signals corresponding to two methylene groups as complex multiplets and not as triplets, and once more confirmed the presence of an uncyclized side chain.



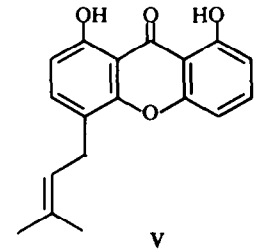
Ia: R = H, R_5 = R_6 = OH, R_7 = H jacareubin
Ib: R = H, R_5 = R_6 = H, R_7 = OH osajaxanthone
Ic: R = H, R_6 = OH, R_6 = R_7 = H 6-dehydroxyjacareubin
Id: R = H, R_5 = OMe, R_6 = R_7 = H
Ie: R = Me, R_5 = OMe, R_6 = R_7 = H



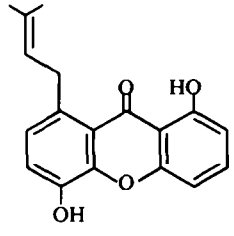
IIa: R = H guanandin
IIb: R = Me



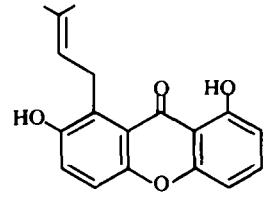
IVa: R = H
IVb: R = Me



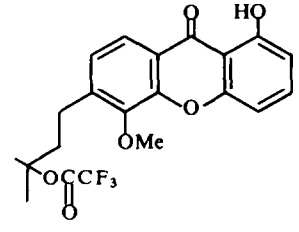
V



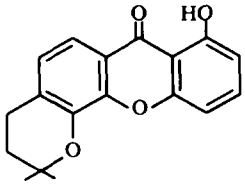
III isoguanandin



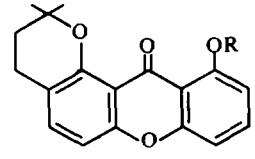
VI



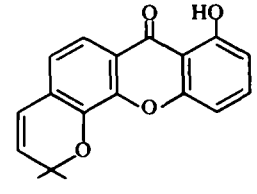
IX



VII cycloguanandin



VIIIa: R = H
VIIIb: R = Me



X dehydrocycloguanandin

Dehydrocycloguanandin from Calophyllum brasiliense.[23] Finally, still another constituent of jacareúba wood had a mol wt of 294, two mass units less than that of the guanandin isomers. The presence of a 2',2'-dimethylchromene system was, consequently, suspected and, indeed, loss of a methyl radical as by far the most conspicuous consequence of electron impact[21] favoured this supposition. The NMR spectrum (Table 1), when compared with the spectrum of cycloguanandin (VII), clearly revealed a close structural relationship of both substances. Indeed, cycloguanandin (VII) was obtained by catalytic hydrogenation of the new isolate which, thus, can only have the structure of dehydrocycloguandin (X).

The distribution of the oxygenated functions in all the described natural products conforms to patterns which emerged lately as quite general for xanthones of dicotyledons and should have biosynthetic implications.[24] The co-occurrence of guanandin (IIa) and of dehydrocycloguanandin (X) lends further support to the suggestion that oxydative cyclization of an isoprenyl side chain is involved in the formation of the 2,2-dimethylchromenes.[25, 26]

TABLE 2. UV SPECTRA OF 1,n-DIHYDROXYXANTHONES IN EtOH

Compound[a]	λ_{max} in mμ (ε × 10^{-3})				
Guanandin	235 sh (15·5)	252 (28·0)		316 (7·5)	372 (3·0)
Isoguanandin	235 sh (25·7)	251 (40·4)		320 (8·7)	376 (5·0)
1,5-Dihydroxyxanthone	237 sh (19·9)	247 (30·4)		316 (4·6)	374 (1·8)
1,2-Dihydroxyxanthone	244 (18·8)	261 (19·4)		290 sh (8·0)	385 (2·8)
1,3-Dihydroxyxanthone	236 (20·4)	254 (13·7)		308 (8·8)	349 (4·4)
1,4-Dihydroxyxanthone	229 (22·1)	263 (24·3)		299 (6·7)	390 (3·5)
1,6-Dihydroxyxanthone	230 (19·8)	247 (12·3)	264 (6·6)	304 (7·3)	365 (3·7)
1,7-Dihydroxyxanthone	235 (38·5)	260 (40·3)		288 (7·5)	
1,8-Dihydroxyxanthone	230 (22·8)	250 (35·1)	280 (2·5)	330 (11·4)	380 (5·4)

[a] We are indebted to Dr. F. Scheinmann, University of Salford, Lancashire, England, for samples of 1,5-dihydroxyxanthone and 1,6-dihydroxyxanthone. All other reference compounds were obtained in the course of the present work.

EXPERIMENTAL

M.ps were determined using a Kofler hot stage microscope and are uncorrected. Separations by column chromatography were carried out using 50 times the wt of the mixture of Merck Kieselgel 0·05–0·20 mm. Elutions were performed successively with pet. ether–benzene, benzene, benzene–$CHCl_3$, $CHCl_3$ and $CHCl_3$–MeOH. Pet. ether refers to b.p. 45–75°. TLC employed Merck Kieselgel G. IR spectra were

determined using a Perkin–Elmer Infracord model 137B spectrometer. Only major bands are quoted. UV spectra were determined on 95% EtOH solns, using a Beckman DU spectrophotometer. Mass spectra were obtained with an Associated Electrical Industries instrument model MS-9, operating at an ionizing voltage of 70 eV. Data refer to *m/e*. Percentage abundance of ions with reference to base peak are in brackets. Only peaks with an intensity of over 15% of the base peak are quoted.

Isolation of osajaxanthone from Kielmeyera corymbosa. The wood, collected in the cerrado region near Belo Horizonte, Minas Gerais State, was separated from its bark, reduced to powder (8·6 kg) and extracted with EtOH in a Soxhlet type apparatus. The concentrated ethanolic soln was washed with pet. ether and extracted with benzene. The concentrated benzene soln was filtered and washed successively with $NaHCO_3$aq, Na_2CO_3aq and 3% NaOHaq. The NaOH-solubles were precipitated with HCl and extracted into $CHCl_3$. The $CHCl_3$ soln was dried and its evaporation residue (4·3 g) subjected to column chromatography. The $CHCl_3$–MeOH (49:1) fractions yielded, upon evaporation, crude osajaxanthone (15 mg).

Isolation of 6-dehydroxyjacareubin from Kielmeyera speciosa. The wood, collected in the cerrado region near Brasilia, Distrito Federal, was separated from its bark, reduced to powder (12 kg) and extracted with benzene in a Soxhlet type apparatus. The concentrated benzene soln was filtered, evaporated and the residue extracted with pet. ether. The pet. ether soln was washed successively with $NaHCO_3$aq, Na_2CO_3aq and 3% NaOHaq. The NaOH-solubles (0·9 g) were elaborated as above. The benzene fractions yielded crude 6-dehydroxyjacareubin (10 mg).

Isolation of jacareubin, 6-dehydroxyjacareubin, guanandin, isoguanandin and dehydrocycloguanandin from Calophyllum brasiliense. The wood, collected at Serra do Cipó, Minas Gerais State, was separated from its bark, reduced to powder (3·0 kg) and extracted with benzene. Upon concentration of the benzene soln precipitated crude jacareubin, which was separated by filtration. From this jacareubin (4 g; m.p. 254–256°, lit.[13] 254–256°) was obtained by recrystallizations from EtOH–water. The benzene soln was evaporated and the residue subjected to column chromatography. The pet. ether–benzene (4:6) fractions yielded crude dehydrocycloguanandin (20 mg), the pet. ether–benzene (3:7) fractions crude guanandin (100 mg), the pet. ether–benzene (1:9) fractions crude isoguanandin (40 mg) and the benzene fractions crude 6-dehydroxyjacareubin (200 mg).

Osajaxanthone. Compound Ib was obtained after recrystallizations from EtOH as yellow needles, m.p. 249–252°, lit.[27] 264–265°. λ_{max} 238, 249, 286, 339, 382 mμ (ε resp. 19,000; 18,000; 47,100; 8200; 4800); no alteration in presence of NaOAc; λ_{max}^{NaOH} 243, 302 mμ (ε resp. 25,400; 43,500); $\lambda_{max}^{AlCl_3}$ 235, 289, 349 mμ (ε resp. 19,600; 38,400; 8300). ν_{max}^{Nujol} 3230, 1638, 1612, 1580, 822 cm^{-1}. Gibbs test positive. λ_{max} 695 mμ (ε 3300). Ferric chloride test positive. Mol. wt. (mass spectrum) 310.

6-Dehydroxyjacareubin. Compound Ic was obtained, after recrystallizations from benzene, as yellow plates, m.p. 211–213°. λ_{max} 240, 250, 286, 309, 369 mμ (ε resp. 19,000; 18,900; 42,600; 19,600; 4000); λ_{max}^{NaOAc} 280, 296, 320 sh, 385 mμ (ε resp. 35,900; 35,400; 12,900; 3400); λ_{max}^{NaOH} 255, 297, 344 mμ (ε resp. 19,700; 37,400; 14,900); $\lambda_{max}^{AlCl_3}$ 240, 251, 290, 305 sh, 348 mμ (ε resp. 18,900; 19,700; 37,900; 28,200; 10,000). ν_{max}^{Nujol} 3340, 1655, 1618, 1580, 1300, 1225, 1185, 1137, 1095, 835, 760 cm^{-1}. NMR spectrum Table 1. Mass spectrum 310 (25·4), 295 (100·0).

5-O-Methyl-6-dehydroxyjacareubin. Compound Ic was treated with excess ethereal diazomethane soln overnight. Evaporation of the reaction mixture and recrystallization of the residue from benzene–cyclohexane (2:8) yielded yellow needles (Id), m.p. 170–172°. λ_{max} 239, 249 sh, 265 sh, 285, 290 sh, 310 sh mμ (ε resp. 20,000; 19,400; 25,600; 39,000; 38,800; 18,000); no alteration in presence of NaOAc; λ_{max}^{NaOH} 246, 310, 405 mμ (ε resp. 24,200; 29,000; 4600); $\lambda_{max}^{AlCl_3}$ 239, 249, 270 sh, 290, 303, 335 mμ (ε resp. 20,000; 19,500; 20,000; 32,000; 28,700; 12,000).

1,5-Di-O-methyl-6-dehydroxyjacareubin. To a soln of Ic (30 mg) in anhyd acetone (15 ml) were added Me_2SO_4 (0·4 ml) and calcinated K_2CO_3 (100 mg). The mixture was maintained under reflux for 18 hr, cooled to room temp and filtered. Evaporation of the solvent left a residue, which was treated with ammonia (0·5 ml) and water (10 ml). The ppt was extracted into $CHCl_3$, which was washed with 3% NaOHaq, dried and evaporated. Recrystallization of the residue from benzene–hexane gave pale yellow needles (Ie), m.p. 196–199°. λ_{max} 240 sh, 275, 330, 352 mμ (ε resp. 17,900; 53,000; 6000; 6700); no alteration in presence of NaOAc, NaOH, $AlCl_3$. NMR spectrum Table 1.

Guanandin. Compound IIa was obtained, after recrystallizations from benzene, as lustrous yellow plates, m.p. 206–208°. λ_{max} Table 2; λ_{max}^{NaOAc} 252, 275 sh, 320, 365 mμ (ε resp. 26,400; 7200; 7300; 2800); λ_{max}^{NaOH} 260, 315, 366 mμ (ε resp. 22,700; 4200; 6500); $\lambda_{max}^{AlCl_3}$ 235 sh, 255, 268 sh, 347 mμ (ε resp. 15,500; 22,000; 16,000; 5900). ν_{max}^{Nujol} 3400, 1650, 1612, 1580, 1280, 1225, 1075, 1050, 900, 805, 700 cm^{-1}. NMR spectrum Table 1.

Mass spectrum 297 (25·0), 296 (100·0), 281 (40·0), 279 (25·0), 253 (17·0), 241 (88·0), 240 (77·5), 128 (47·5), 105 (18·0), 91 (26·0), 81 (21·0).

5-O-Methylguanandin. Guanandin (IIa) was left for several days in an ethereal soln containing an excess of diazomethane. Evaporation of the reaction mixture and recrystallization of the residue from MeOH yielded yellow plates, m.p. 101–101·5°. λ_{max} 235, 245, 294, 366 mμ (ε resp.. 36,200; 37,000; 12,800; 5400); no alteration in presence of NaOAc; λ_{max}^{NaOH} 232 sh, 237, 270, 309 mμ (ε resp. 37,100; 48,400; 22,400; 11,700); $\lambda_{max}^{AlCl_3}$ 235, 268, 275 sh, 310 sh, 319 mμ (ε resp. 35,600; 26,600; 26,300; 11,100; 11,200). Gibbs test positive λ_{max} 670 mμ (ε 2260). ν_{max}^{KBr} 3020 (broad), 1645, 1605, 1570, 1380, 1270, 1235, 1070, 885, 800, 700 cm^{-1}. NMR spectrum Table 1.

Cycloguanandin. A trifluoroacetic acid soln of IIa was heated for 15 min on the steam bath. After the reaction mixture had cooled to room temp, water was added. The ppt was filtered off, washed free of acid, dried, sublimed under vacuum and recrystallized from MeOH, yellow needles (VII), m.p. 165–167°. λ_{max} 235 sh, 254, 316, 368 mμ (ε resp. 24,800; 51,100; 10,000; 5300); no alteration in presence of NaOAc; λ_{max}^{NaOH} 241, 265 sh, 314; 398 mμ (ε resp. 48,100; 17,000; 10,400; 7600; $\lambda_{max}^{AlCl_3}$ 237, 263, 298, 311, 347 mμ (ε resp. 21,700; 35,300; 4500; 4400; 7700). ν_{max}^{KBr} 1650, 1610, 1570, 1450, 1285, 1235, 1075, 795, 695 cm^{-1}.

A soln of X (4 mg) in MeOH (10 ml) was hydrogenated in presence of 10% Pd/C catalyst (1 mg) during 30 min. The soln was filtered and evaporated. The residue was recrystallized from MeOH, yielding yellow needles, identified by direct comparison with cycloguanandin.

Isoguanandin. Compound III was obtained, after recrystallizations from benzene, as yellow plates, m.p. 175–176°. λ_{max} Table 1; λ_{max}^{NaOAc} 252, 275 sh, 323, 381 mμ (ε resp. 38,000; 10,500; 10,100; 4400); λ_{max}^{NaOH} 246, 320, 350 mμ (ε resp. 37,400; 6600; 9600); $\lambda_{max}^{AlCl_3}$ 235 sh, 251, 274 sh, 320, 265 mμ (ε resp. 25,500; 36,000; 8700; 7400; 5100). ν_{max}^{Nujol} 1645, 1595, 1580, 1280, 1075, 825, 740 cm^{-1}. NMR spectrum Table 1. Mass spectrum 296 (41·5), 254 (20·0), 253 (100·0), 241 (20·5).

Dehydrocycloguanandin. Compound X was obtained, after recrystallizations from pet. ether–benzene (1:1) as yellow needles, m.p. 167–169°. λ_{max} 235, 265, 305 sh, 345 mμ (ε resp. 23,500; 22,300; 4800; 15,300); no alteration in presence of NaOAc; λ_{max}^{NaOH} 238, 250, 290, 300 sh, 346 mμ (ε resp. 23,200; 22,100; 10,600; 9400; 10,600); $\lambda_{max}^{AlCl_3}$ 235, 275, 330, 378 mμ (ε resp. 22,000; 19,700; 4600; 10,900). NMR spectrum Table 1. Mass spectrum 294 (26·8), 280 (19·5), 279 (100·0), 139·5 (17·5).

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