Phytochemistry, 1976, Vol. 15, pp. 1553–1558 Pergamon Press. Printed in England.

FLAVONOIDS OF *DERRIS OBTUSA*: AURONES AND AURONOLS

MARIA CÉLIA DO NASCIMENTO, RICARDO LUIZ DE VASCONCELLOS DIAS and WALTER B. MORS

Centro de Pesquisas de Produtos Naturais, Departamento de Bioquímica, Instituto de Ciências Biomédicas, Universidade Federal do Rio de Janeiro, Rio de Janeiro ZC-32, Brazil

(*Received* 27 *February* 1976)

Key Word Index—*Derris obtusa*; *Lonchocarpus obtusus*; Leguminosae; aurones; auronols; 3-*O*-methyl-auronols; derriobtusone A; derriobtusone B; P.M.R.; MS.

Abstract—Heptacosanol and sitosterol, one chalcone, one flavone, one 3-*O*-methyl-flavonol, four aurones and two 3-*O*-methylauronols were isolated from the root bark of *Derris obtusa*. The latter compounds, called Derriobtusones A and B, are the first auronols found in nature. Structures were established through chemical and spectral means. Mass spectral fragmentation schemes are suggested for aurones and auronols.

INTRODUCTION

The genus *Derris* Lour. (including *Lonchocarpus* HBK)*, of the Family Leguminosae, subfamily Lotoideae, is especially interesting from the phytochemical viewpoint, because of the wide range of flavonoids which it has been shown to produce. Chalcones and flavanones [3–9], isoflavones [10–12], 4-hydroxy-3-phenyl-coumarins [11,12], and rotenoids [13] have been found in the root bark of *Derris* species. We now wish to report on the flavonoids present in the root bark of *Derris obtusa* (Benth.) Ducke (= *Lonchocarpus obtusus* Benth.), a tree growing in the Serra da Meruoca, municipality of Sobral, in the state of Ceará, Brazil [14], where it is known under the popular name of "cocão-coringa". Analysis of its root bark provided us with a series of new flavonoids, comprising one chalcone, one flavone, one flavonol, four aurones and two auronols. The latter compounds, being the first auronols found in nature, were named derriobtusones A and B.

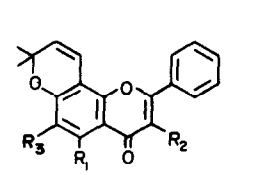
RESULTS AND DISCUSSION

The ground root bark was extracted successively with petrol, Et_2O and EtOH. All compounds described in this paper were isolated from the first two extracts, chromatographed on columns of Si gel and eluted with solvent mixtures starting with petrol and increasing the polarity gradually through toluene, $CHCl_3$ and EtOAc, to MeOH. Derriobtusone A, the major crystalline component, in part crystallized out directly and could still be abundantly isolated from the marc through a subsequent extraction with EtOH. Its total yield was 0.8% of the dry root bark.

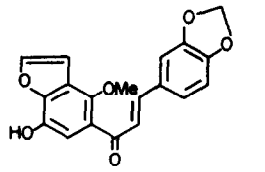
The isolated flavonoids have been numbered **1** to **9** and their order of elution from the columns is given in the Experimental. In accordance with their substitution pattern, the compounds listed can be divided into three groups. Group I: Flavonoids with a dimethylchromene ring attached to ring A and with ring B unsubstituted—compounds **1** and **2**. Group II: Flavonoids with a furan ring attached to ring A and ring B unsubstituted—compounds **3–6**. Group III: Flavonoids with a furan ring attached to ring A and a methylenedioxy-substituent in ring B—compounds **7–9**.

Group I

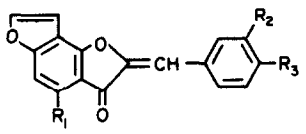
Compounds **1** and **2** are flavones, with **2** bearing a OMe group at C-3, thus being a 3-*O*-methyl-flavonol. UV, IR, PMR and MS are in accord with the proposed structures (for detailed data, see Experimental). The PMR spectrum of **1** (in $CDCl_3$, see Table 1) exhibits the dimethylchromene nucleus with a sharp singlet at 1.54 δ (6 H) due to the *gem* Me groups, and the two olefinic protons appearing as doublets at 5.62 and 6.78 δ. These assignments agree with those previously reported



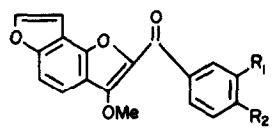
(1) R_1 = OH, R_2 = R_3 = H
(2) R_2 = R_3 = OMe, R_1 = H



(7)

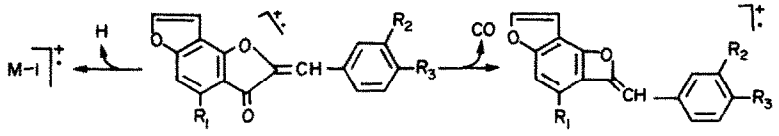


(3) R_1 = R_2 = R_3 = H
(4) R_1 = OH, R_2 = R_3 = H
(5) R_1 = OMe, R_2 = R_3 = H
(8) R_1 = H, R_2 + R_3 = O–CH_2–O

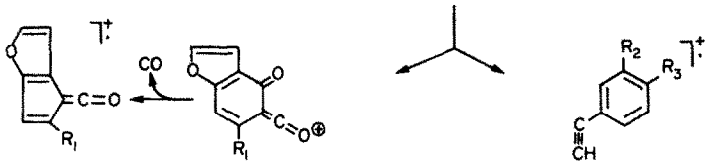


(6) R_1 = R_2 = H
(9) R_1 + R_2 = O–CH_2–O

* Fusion of the two genera was suggested by J. F. MacBride, in 1943 [1] and accepted by A. Ducke for the Brazilian species [2].



	m/e	%	M^+	%	*m/e*	%
3	261	6	262	100	234	21
4	277	3	278	100	250	3
5	291	31	292	100	264	21
8	305	13	306	95	278	3
Sulphuretin	269	53	270	100	242	8



	m/e	%	*m/e*	%	*m/e*	%
3	132	26	160	39	102	17
4	148	8	176	75	102	9
5	162	6	190	4	102	11
8	132	20	160	74	146	100
Sulphuretin	108	6	136	5	134	15

Scheme 1. Principal mass spectral fragmentations of aurones

by us for flavonoids bearing the same structural feature [3,4]. The typical flavone proton, at C-3, in **1** shows up as a singlet at 6.28 δ, and the chelated OH group resonates as another singlet, downfield, at 12.78 δ. The proton at C-6, in turn, is well characterized as a singlet (1 H) at 7.64 δ.

MS fragments are few, rather typical for a flavone, with the M^+-14 ion predominating (*m/e* 306; 100%), the next most abundant fragment being the substituted benzoyl from ring A (*m/e* 203; 41%).

The PMR spectrum of **2** has some signals in common with that of **1**, although it lacks signals for the protons at C-3 and the OH group, but exhibits instead two OMe at 3.90 δ (3 H) and 3.98 δ (3 H). Treatment with HI leads to cleavage of both Me ethers and reduction of the chromene double bond.

Groups II and III

The flavonoids of these groups comprise one chalcone, four aurones and two 3-*O*-methyl auronols. The three aurones of group II are similar in structure, differing in the substituents, or absence of substituents, at C-5. All exhibit the benzylic proton resonance in the vicinity of 6.80 δ (*s*, 1 H) and two multiplets corresponding to protons a and b of the furan ring, centered around 7.7 δ and 7.1 δ, respectively. Features due to substitution at C-5 are as expected. Aurones **4** and **5** could be easily interconverted by means of their respective methylation and demethylation.

The fourth aurone (**8**) belongs to group III; its PMR spectrum resembles closely that of compound **5**, differing solely in the alterations introduced by the presence of the methylenedioxy substituent in ring B. These comprise primarily the singlet at 6.10 δ due to the CH_2 protons, as well as the doublet-rich pattern which arises from disruption of the hydrogen sequence of the benzene ring.

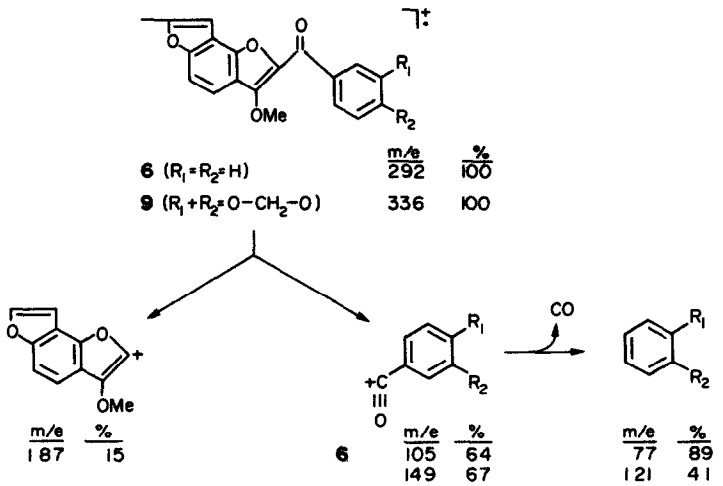
The isolation of four new aurones from a single plant is in itself noteworthy, increasing the number of known natural members of this class from 8 to 12. At the same time, it offered the opportunity of studying the MS fragmentation of aurones, on which there is a scarcity of information. Scheme 1 presents a general view of the six main peaks which consistently appear in all the spectra, in a suggested fragmentation pattern*. One previously known aurone, sulphuretin, has been included for comparison†.

By far the most interesting constituents of the plant are the two methylated auronols, **6** and **9**. Just over ten years ago, Hänsel *et al.* [15] proposed an auronol (aroylcoumaranone) structure for *Helichrysum* compound B, earlier isolated by Vrkoč *et al.* [16] from the flower heads of *Helichrysum arenarium* DC. Shortly afterwards, however, they reconsidered their claim, having identified the substance as a flavonol [17]. In fact, their earlier degradative evidence appeared to fit equally well the proposed auronol structure, and an attempted proof of structure by synthesis was misleading, since flavonols result as byproducts in the Geissman-Armen synthesis of auronols [18,19]. With the auronol derivatives **6** and **9** isolated in this investigation, ambiguities of this kind could be definitely excluded.

Apart from spectral data (see Table 1 and Scheme 2), acid hydrolysis offers the best proof of structure. Thus, derriobtusone A (**6**) is easily demethylated by dil HCl under reflux, yielding the corresponding auronol (**10**) after 15–30 min. Continued boiling degrades **10** into the furanocoumaranone **11** and benzoic acid. Under the same conditions, derriobtusone B (**9**) behaves in an identical fashion yielding only piperonylic acid as the product

* A confirmation of the proposed fragmentation path is at present being investigated at this Laboratory through the identification of metastable peaks by means of the DADI technique.

† We thank Dr. J. B. Harborne, University of Reading, U.K., for a sample of sulphuretin (synthetic, mp 280–285°).



Scheme 2. Principal mass spectral fragmentation of 3-*O*-methyl-auronols: Derriobtusones A (**6**) and B (**9**).

arising from ring B. Such evidence would in itself be sufficient to preclude the flavonol structure which, in the case of the *Helichrysum* substance, proved to be the correct one. Furthermore, in the present case, the two corresponding isomers of flavonol structure are known compounds, differing in every respect from the two derriobtusones. Karanjin (**12**) [20] and pongapin (**13**) [21], originally described in several Indian *Pongamia* species, were available to us for a direct comparison because of their occurrence in the Brazilian tree, *Dahlstedtia pinnata* (Benth.) Malme [22]. Both were resistant to acid, undergoing demethylation only on treatment with HI [20] or HBr [23]. Spectral data of the two 3-*O*-methyl-auronols (Scheme 2, Table 1 and Experimental Part) are in agreement with the proposed structures.*

An interesting physical property of derriobtusone A is its extraordinary tendency to crystallize in large, cream-coloured, crystals of the triclinic system. Crystals measuring several centimeters in width formed spontaneously from concentrated EtOH solution. Their crystallographic study, undertaken by J. P. and J. O. Cassedanne of the Department of Earth Sciences of the Federal University of Rio de Janeiro, will be published elsewhere.

In view of some of the new structures presented, some accepted generalizations will have to be revised. Bohm [24] considers a resorcinol-type A-ring in the anthochlor pigments a biochemical characteristic of the Leguminosae. With the addition of flavones **1** and **2** and aurones **4** and **5**, of the phloroglucinol type, to the one previously known exception (xanthohumol in the roots of *Sophora angustifolia*), the above statement can no longer be considered valid. The same author calls attention to the fact that at the time of his review of the subject no naturally occurring aurones were known which lacked B-ring OH functions. Also this observation is overruled by the isolation of the aurones (and, if one wishes, also the auronols) from *Derris obtusa*.

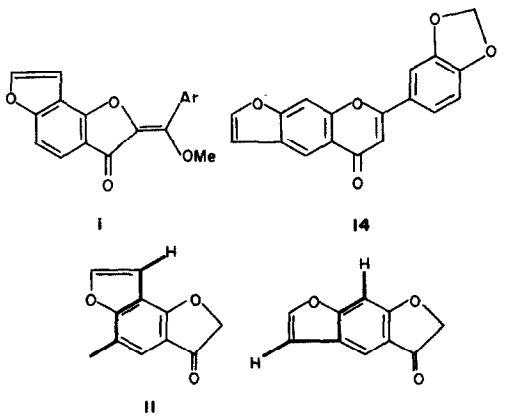
EXPERIMENTAL

Mps were determined on the Kofler hot stage. UV spectra were obtained in 95% EtOH and IR spectra in KBr. PMR spectra were measured at 100 MHz and MS at 70 eV.

Extraction. Ground root bark of *D. obtusa* was exhaustively percolated with petrol (bp 40–80°) and the combined extracts were concentrated, whereupon crystals separated out. These were filtered and later identified as **6**. The marc, after drying, was subjected to a second exhaustive percolation with Et_2O. TLC comparison of the two extracts showed no significant difference; they were therefore combined for further processing. The combined extractives (60 g) were redissolved in petrol, adsorbed on 30 g of Si gel 60 (Merck), and after evaporation of the solvent, placed on top of a column of 1.5 kg

* The conceivable alternative structure **i** could be eliminated on account of the mass fragment *m/e* 187.0343, confirmed in both compounds by high resolution ($C_{11}H_7O_3$ requires 187.0394).

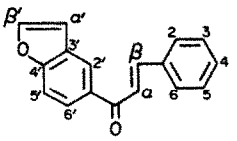
Another possibility—the linear arrangement of the fused furan ring—such as occurs, e.g. in pinnatin (**14**), was dismissed with the aid of the Varian NMR spin simulation program. In both the linear and angular benzofuran structures long distance coupling occurs over five bonds, as shown:



Spin interaction of such coupling with the rest of the molecule leads to different spectra. A simulation program, set up using the coupling diagram and chemical shifts of known benzofuran systems generated for the angular pattern a spectrum which, though simplified, was essentially identical with that of the degradation product **11**. We are grateful to Mr. Antonio Jorge Ribeiro da Silva for his collaboration in solving this question.

Table 1. PMR data of

Numbering of nuclei:



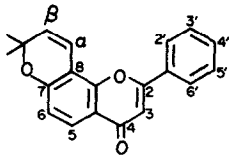
Group	Chalcone 7	Flavone 1	Flavone 2	*Chalcone* Aurone 3
Hydroxyl, chelated	—	12.78 (1H, *s*, C-5)	—	—
Methoxyl	4.14(3H, *s*, C-2')	—	3.98(3H, *s*, C-6)	—
			3.90(3H, *s*, C-3)	—
Dimethylchromene				
Gem-dimethyl	—	1.54(6H, *s*, C-γ)	1.58(6H, *s*, C-γ)	—
Methynic protons	—	6.78(1H, *d*, J = 10 Hz, C-α)	6.88(1H, *d*, J = 10 Hz, C-α)	—
		5.62(1H, *d*, J = 10 Hz, C-β)	5.75(1H, *d*, J = 10 Hz, C-β)	—
Furan	7.84(1H, *d*, J = 2 Hz, C-β')	—	—	7.74(1H, *d*, J = 2 Hz, C-β)
	6.98(1H, *q*, J = 2 Hz, C-α')	—	—	7.14(1H, *q*, J = 2 Hz, C-α)
Methylenedioxy	6.06(2H, *s*)	—	—	—
Aromatic	7.30–7.70(3H, *m*, C-2, 6)	7.84–7.92(2H, *m*, C-2',6')	8.02–8.12(2H, *m*, C-2',6')	8.14(1H, *d*, J = 9 Hz, C-4)
	7.40(1H, *s*, C-6')	6.64(1H, *s*, C-6)	7.50–7.54(3H, *m*, C-3',4',5')	7.84–7.98(2H, *m*, C-2',6')
	6.88(1H, *d*, C-5)	7.46–7.60(3H, *m*, C-3',4',5')	7.48(1H, *d*, J = 8 Hz, C-5)	7.80(1H, *d*, J = 8 Hz, C-5)
				7.42–7.60(3H, *m*, C-3',4',5')
Styryl	7.62(1H, *d*, J = 10 Hz, C-β)	—	—	—
	7.32–7.44(1H, *d*, J = 10 Hz, C-α)	—	—	—
Benzyl	—	—	—	6.84(1H, *s*)
Isolated proton	—	6.28(1H, *s*, C-3)	—	—

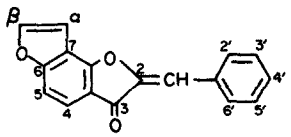
*Chemical shifts in δ units, with spectra scanned up to $\delta = 16$; solvent $CDCl_3$ with TMS as internal standard ($\delta = 0$).

of the same adsorbent. Elution was started with petrol and the polarity of the eluent increased gradually. Compounds were eluted in the following order, although in the first chromatographic fractionation the separation was not clearcut, often requiring purification on smaller columns or by preparative-TLC:

Heptacosanol. Eluted with hexane. White powder, mp 79. IR: ν_{max} cm^{-1}: 3390 (broad), 720. MS: *m/e* 396 (M^+, 10), 382 (8), 368 (100), 354 (13), 340 (21). *Methylenedioxy-(3,4)-5'-hydroxy-2'-methoxy-furano-4',3',2'',3'')-chalcone* (**7**). Eluted with hexane–toluene (9:1). Yellow needles from EtOH, mp 118°. IR: ν_{max}cm^{-1}: 1639 (>C=O). UV: λ_{max}^{EtOH} nm (log ε): 362 (4.53), 237 (4.53). MS: *m/e* 338 (M^+, 15), 308 (19), 307 (100), 175 (41), 160 (21), 149 (40), 148 (20). Found, *m/e* 338.0809; $C_{19}H_{14}O_6$ requires 338.0786. For PMR data, see Table 1. *Derriobtusone A* (**6**). Eluted with hexane–toluene (1:7). Large, cream-coloured crystals from EtOH, mp 132°. Anal.: Found: C 73.35, H 4.12, OMe 10.99; Calc. for $C_{18}H_{12}O_4$: C 73.96, H 4.14, OMe 10.62. IR: ν_{max}cm^{-1}: 1640 (>C=O), 1250, 750, 700. UV: λ_{max}^{EtOH} nm (log ε): 327 (6.06), 263 (5.99), 258 (6.02), no shift in alkali. For MS and PMR data, see Scheme 2 and Table 1. *4-Hydroxy-furano-(6,7,2'',3'')-aurone* (**4**). Eluted with hexane–toluene (1:9). Dark yellow crystals from EtOH, mp 208–209°. IR: ν_{max} cm^{-1}: 3450 (OH···), 1635 (>C=O), 720, 670. UV: λ_{max}^{EtOH} nm (log ε): 355 (3.51), 282 (4.82), 252 (4.46), 224 (4.67). MS: *m/e* 278 (M^+, 100), 279 (M^+ + 1, 26), 176 (75), 120 (10), 92 (19), 76 (11). Found: *m/e* 278.0591; $C_{17}H_{10}O_4$ requires 278.0578. For PMR data, see Table 1. *5-Hydroxy-6'',6''-dimethylchromeno-(7,8,2'',3'')-flavone* (**1**). Eluted with toluene. Yellow needles from EtOH, mp 170–172°. Anal.: Found: C 74.21, H 4.92; Calc. for $C_{20}H_{16}O_4$: C 74.99, H 5.03. IR: ν_{max}cm^{-1}: 3448 (OH···), 1640 (>C=O), 1372, 1348 (*gem*-diMe), 749, 710. UV: λ_{max}^{EtOH} nm (log ε): 362 (3.60), 279 (4.55), 237 (4.32). MS: *m/e* 320 (M^+, 25), 305 (100), 203 (41), 153 (10). For PMR data, see Table 1. *Derriobtusone* B (**9**). Eluted with toluene. Slightly yellowish crystals from EtOH, mp 145°. IR: ν_{max}cm^{-1}: 1639 (>C=O), 1330, 1020. UV: λ_{max}^{EtOH} nm (log ε): 340 (4.41), 315 (4.27), 267 (4.19), 240 (4.39), 224 (4.43). Found *m/e* 336.0633; $C_{19}H_{12}O_6$ requires 336.0632. For MS and PMR data, see Scheme 2 and Table 1. *Sitosterol.* Eluted with $CHCl_3$. Colourless plates from EtOH, mp 148–151°. MS: *m/e* 414 (M^+, 9), 400 (3), 399 (2), 396 (3), 303 (3), 300 (2), 273 (3), 261 (6), 255 (9), 213 (6), 17 (100). TLC, mmp and IR, identical with an authentic sample. *Furano-(6,7,2'',3'')-aurone* (**3**). Eluted with $CHCl_3$. Slightly yellowish crystals from EtOH, mp 134°. IR: ν_{max}cm^{-1}: 1613 (>C=O), 720, 670. UV: λ_{max}^{EtOH} nm (log ε): 295 (3.71), 267 (3.87), 222 (3.93). MS: *m/e* 262 (M^+, 66), 234 (21), 161 (14), 160 (100), 132 (26), 104 (29), 102 (17), 77 (14), 76 (90), 75 (13). Found *m/e* 262.0578; $C_{17}H_{10}O_3$ requires 262.0629. For PMR data, see Table 1. *3,6-Dimethoxy-6'',6''-dimethylchromeno-(7,8,2'',3'')-flavone* (**2**). Eluted with $CHCl_3$–EtOAc (19:1). Colourless needles from EtOH, mp 205°. Anal: Found: C 72.89, H 5.97, OMe 26.48. Calc. for $C_{22}H_{20}O_5$: C 72.51, H 5.53, OMe 25.55. IR: ν_{max}cm^{-1}: 1629 (>C=O), 1403, 1385 (*gem*-diMe), 730, 694. UV: λ_{max}^{EtOH} nm (log ε): 342 (3.30), 280 (3.31), 250 (3.81), 235 (3.82). MS: *m/e* 364 (M^+, 83), 365 (M^+ + 1, 22), 363 (70), 350 (22), 349 (100), 217 (15), 175 (17), 174 (16), 105 (18), 91 (17), 77 (17), 69 (15). For PMR data, see Table 1. *4-Methoxy-furano-(6,7,2'',3'')-aurone* (**5**). Eluted with $CHCl_3$–EtOAc (19:1). Yellowish needles from EtOH, mp 179°. IR: ν_{max}cm^{-1}: 1637 (>C=O), 722, 680. UV: λ_{max}^{EtOH} nm (log ε): 337 (3.93), 305 4.29), 268 (4.66), 221 (4.48). MS: *m/e* 292 (M^+, 100), 293 (M^+ + 1, 25), 291 (31), 264 (21), 263 (94), 247 (13), 246 (53), 161 (14), 160 (36), 147 (18), 131 (11), 132 (26), 117 (11), 105 (14), 77 (15), 76 (19). Found, *m/e* 292.0745; $C_{18}H_{12}O_4$ requires 292.0734. For PMR data, see Table 1. *Methylenedioxy-(3',4')-furano-(6,7,2'',3'')-aurone* (**8**). Eluted with $CHCl_3$–EtOAc (19:1). Slightly yellow crystals from EtOH, mp 232–233°. Anal.: Found: C 70.03, H 3.56; Calc. for $C_{18}H_{10}O_5$: C 70.59, H 3.29. IR:

flavonoids from *Derris obtusa**





Flavones (and flavonols) Aurone 4	Aurone 5	*Aurones (and auronols)* Aurone 8	Auronol 6 Derriobtusone A	Auronol 9 Derriobtusone B
12.68(1H, *s*, C-4)	—	—	—	—
—	4.22(3H, *s*, C-4)	—	—	—
—				
—	—	—	—	—
—	—	—	—	—
7.72(1H, *d*, *J* = 2 Hz, C-β)	7.62(1H, *d*, *J* = 2 Hz, C-β)	7.76(1H, *d*, *J* = 2 Hz, C-β)	7.71(1H, *d*, *J* = 2 Hz, C-β)	7.62(1H, *d*, *J* = 2 Hz, C-β)
7.08(1H, *q*, *J* = 2 Hz, C-α)	7.08(1H, *q*, *J* = 2 Hz, C-α)	7.18(1H, *q*, *J* = 2 Hz, C-α)	7.09(1H, *q*, *J* = 2 Hz, C-α)	7.08(1H, *q*, *J* = 2 Hz, C-α)
—	—	6.10(2H, *s*)	—	6.08(2H, *s*)
7.90–8.00(2H, *m*, C-2',6')	7.88–7.98(2H, *m*, C-2',6')	8.18(1H, *d*, *J* = 9 Hz, 10 Hz, C-4)	7.98–8.10(2H, *m*, C-2',6')	7.68(1H, *d*, *J* = 8 Hz, C-4)
7.50–7.60(3H, *m*, C-3',4',5')	7.50–7.58(3H, *m*, C-3',4',5')	7.48(1H, *d*, *J* = 8 Hz, C-5)	7.50–7.62(3H, *m*, C-3',4',5')	7.42–7.70(2H, *m*, C-2',6')
6.94(1H, *d*, *J* = 8 Hz, C-5)	7.40(1H, *d*, *J* = 8 Hz, C-5)	7.40–7.70(2H, *m*, C-2',6')	7.48(1H, *d*, *J* = 9 Hz, C-5)	7.44(1H, *d*, *J* = 8 Hz, C-5)
		6.94(1H, *d*, *J* = 8 Hz, C-5')		6.94(1H, *d*, *J* = 8 Hz, C-5')
—	—	—	—	—
—	—	—	—	—
6.84(1H, *s*)	6 72(1H, *s*)	6.80(1H, *s*)	—	—
—	—	—	—	—

ν_{max}cm^{-1}: 1626 (>C=O). UV: λ_{max}^{EtOH} nm (log ε): 330 (4.46), 245 (4.00), 224 (4.65). MS: *m/e* 306 (M^+, 95), 307 (M^+ + 1, 19), 305 (13), 160 (74), 146 (100), 145 (40), 139 (17), 138 (13), 132 (20), 104 (13), 87 (14), 76 (37). For PMR data, see Table 1.

Demethylation of **6**. *Furano-(6,7,2'',3'')-auronol* or *2-benzoyl-furano-(6,7,2',3')-coumaran-3-one* (**10**). 500 mg **6** were heated under reflux in 30 ml aq EtOH (2:1) containing 2 ml conc HCl. Monitoring by means of TLC showed the appearance of a new spot, and maximum yield was obtained after 2.5 hr. On cooling, **10** crystallized directly from the reaction mixture. Yellow needles, mp 178°. UV: λ_{max}^{EtOH} nm (log ε): 375 (5.22), 317 (4.55), 235 (4.84), 220 (5.22). PMR (100 MHz, $CDCl_3$): δ 7.77 (1H, *d*, *J* = 2 Hz, C-α), 7.12 (1H, *q*, *J* = 2 Hz, C-β), 11.20 (1H, *s*, OH···O=C), 7.76 (1H, *d*, *J* = 9 Hz, C-5), 7.48 (1H, *d*, *J* = 9 Hz, C-6), 8.30–8.42 (2H, *m*, C-2',6'), 7.50–7.60 (3H, *m*, C-3',4',5'). MS: *m/e* 278 (M^+, 100), 279 (M^+ + 1, 32), 277 (95), 221 (17), 201 (38), 200 (59), 165 (12), 145 (27), 144 (40), 139 (17), 115 (19), 105 (50), 89 (27), 77 (94), 69 (28), 63 (17). Found: *m/e* 278.0582; $C_{17}H_{10}O_4$ requires 278.0578.

Acid hydrolysis of **10**. *Furano-(6,7,2',3')-coumaran-3-one* (**11**) *and benzoic acid*. The same reaction (see above), carried out for 5.5 hr, produced two new spots on TLC. The mixture was taken to dryness under red press and the residue chromatographed on a small column of Si gel 60 (Merck). First eluted was compound **11**, dark yellow needles, mp 93°. UV: λ_{max}^{EtOH} nm (log ε): 325 (5.78), 272 (5.84), 258 (5.87), 245 (6.26), 230 (6.50). PMR (100 MHz, $CDCl_3$): δ 4.70 (2H, *s*, $-CH_2O-$). MS: *m/e* 174 (M^+, 100), 173 (M^+–1, 26), 160 (11), 146 (26), 145 (15), 144 (15), 118 (18), 117 (78), 116 (94), 90 (11), 89 (35), 88 (24), 87 (50), 86 (15), 64 (20), 63 (33). Found, *m/e* 174.0327; $C_{10}H_6O_3$ requires 174.0315. *Benzoic acid* was identified by comparison (TLC, mp, mmp, IR) with an authentic sample.

Acid degradation of **9**. *Furano-(6,7,2',3')-coumaran-3-one* (**11**) and piperonylic acid. 20 mg of **9** were heated for 5.5 hr under reflux in 15 ml aq EtOH (2:1) containing 1 ml conc HCl. Upon concentration, crystals separated out, showing two spots on TLC. Preparative-TLC cn Si gel afforded **11** and *piperonylic acid*, both identified by comparison with authentic specimens.

Interconversion of aurones **4** *and* **5**. *Demethylation of* **5**. 25 mg of **5** were dissolved in 15 ml conc HBr and heated under reflux for 48 hr. On colling, crystals of **4** separated, were filtered and recrystallized from EtOH. mp 206–208°. *Methylation of* **4**. 30 mg of **4** were dissolved in 15 ml of dry Me_2CO and 250 mg of Me_2SO_4 and 250 mg dry K_2CO_3 added. After 28 hr heating under reflux the mixture was cooled and filtered and the K_2CO_3 was washed with dry Me_2CO(×3). The filtrate was evaporated to dryness, *in vacuo*. and the residue dissolved in $CHCl_3$ and the soln washed once with NH_4OH and twice with H_2O. The organic layer, filtered and taken to dryness, under red press, without heating. Crystals from EtOH, mp 179–182°, identified as **5**.

Acknowledgements—The authors gratefully acknowledge the financial support received from the Financiadora de Estudos e Projetos, Ministry of Planning; Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazilian National Research Council); Coordenação do Aperfeiçoamento do Pessoal de Nivel Superior (Agency for Training, Ministry of Education); and Conselho de Pesquisas da UFRJ (Research Council of the Federal University of Rio de Janeiro). They are also grateful to Dr. Afrânio G. Fernandes, of the Institute of Biology of the Federal University of Ceará for collection and identification of the plant material, and to Dr. P. M. Baker and his staff at the "Central Analítica" of the CPPN, Federal University of Rio de Janiero, for obtaining the spectra and to the Laboratory A. Bernhardt, Elbach, W. Germany for elemental analyses.

REFERENCES

1. MacBride, J. F. (1943) *Flora of Peru*, Chicago Field Museum of Natural History, Botanical Series XIII (III) No. 1.
2. Ducke, A. (1949) *Bol. Téc. Inst. Agron. Norte* (*Belém*), No. 18, 195.

3. Nascimento, M. C. and Mors, W. B. (1970) *An. Acad. Brasil. Ciênc.* **42,** (Suppl.), 87.
4. Nascimento, M. C. and Mors, W. B. (1972) *Phytochemistry* **11,** 3023.
5. Gonçalves de Lima, O., Marini-Bettòlo, G. B., Mello, J. F., Delle Monache, F., Barros Coelho, J. S., Andrade Lyra F. D. and Albuquerque, M. M. F. (1973) *Acad. Naz. Lincei (Ser.* 8) **53,** 433.
6. Gonçalves de Lima, O., Marini-Bettòlo, G. B., Mello, J. F., Delle Monache, F., Barros Coelho, J. S., Andrade Lyra, F. D. and Albuquerque, M. M. (1973) *Gazz. Chim. Ital.* **103,** 771.
7. Delle Monache, G., Mello, J. F., Delle Monache, F., Marini-Bettòlo, G. B., Gonçalves de Lima, O. and Barros Coelho, J. S. (1974) *Gazz, Chim. Ital.* **104,** 861.
8. Braz Filho, R., Gottlieb, O. R. and Mourão, A. P. (1975) *Phytochemistry* **14,** 261.
9. Braz Filho, R., Gottlieb, O. R., Mourão, A. P., Rocha A. I. and Oliveira F. S. (1975) *Phytochemistry* **14,** 1454.
10. Harper, S. H. (1940) *J. Chem. Soc.* 1178.
11. East, A. J., Ollis, W. D. and Wheeler, R. E. (1969) *J. Chem. Soc.* (C) 365.
12. Falshaw, C. P., Harmer, R. A. Ollis, W. D., Wheeler, R. E., Lalitha, V. R. and Subba Rao, N. V. (1969) *J. Chem. Soc.* (C), 374.
13. Feinstein, L. and Jacobson, M. (1953) *Progr. Chem. Org. Nat. Prods.* **10,** 423.
14. Ducke, A. (1959) *An. Acad. Brasil. Ciênc.* **31,** 275.
15. Hänsel, R., Rimpler, H. and Schwarz, R. (1965) *Tetrahedron Letters* No. 21, 1545.
16. Vrkoč, J., Herout, V. and Sǒrm, F. (1959) *Coll. Czech. Chem. Commun.* **24,** 3938.
17. Hänsel, R., Rimpler, H. and Schwarz, R. (1967) *Tetrahedron Letters* No. 8, 735.
18 Geissman, T. A. and Armen, A. (1955) *J. Am. Chem. Soc.* **77,** 1623.
19. Gottlieb, O. R. (1975) Flavonols in *The Flavonoids* (Harborne, J. B., Mabry, T. J. & Malbry, H., eds.) p. 356. Chapman & Hall, London.
20. Manjunath, B. L. (1939) *Ber. Deut. Chem. Ges.* **72,** 93.
21. Row, L. R. (1953) *Chem. Abstr.* **47,** 12372.
22. Nascimento, M. C., Tomassini, E. B. and Mors, W. B.: Unpublished results; presented at the 27th Annual Meeting of the Sociedade Brasileira para o Progresso da Ciência, Belo Horizonte, July 9–16, 1975.
23. Krishnaswamy, B. and Seshadri, T. R. (1942) *Proc. Indian Acad. Sci.* **15A,** 437; *Chem. Abstr.* **36,** 7024.
24. Bohm, B. A. (1975) Chalcones, aurones and dihydrochalcones in *The Flavonoids* (Harborne, J. B., Mabry, T. J. & Mabry, H., eds,) pp. 442–504. Chapman & Hall, London.