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LIMONOIDS FROM *ATALANTIA MONOPHYLLA*

ISOLATION AND STRUCTURE

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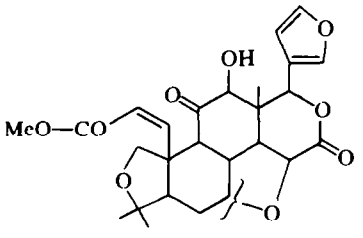
Abstract—The isolation and structure determination of three limonoids from *Atalantia monophylla* (Rutaceae) is described. One of these is the previously reported atalantin and the others, dehydroatalantin and cycloepiatalantin, are structurally related. These limonoids have been chemically interrelated. Evidence leading to revised structures for atalantin and dehydroatalantin is presented. The chemical and spectroscopic evidence, including ^{13}C NMR, indicate structures **7**, **8** and **11**, respectively, for the limonoids.

Atalantia (Rutaceae) is a genus of eleven species which is closely related to *Citrus*.[1] Three species of *Atalantia* have been the subject of chemical studies. Coumarins[2,3] acridone alkaloids,[4,5] triterpenes,[3] sesquiterpenes[6] and limonoids[5-7] have been reported. Three limonoids, atalantin (**1**), dehydroatalantin (**2**) and atalantolide (**3**) have been reported[5-7] to occur in *A. monophylla*. The proposed structures[6,7] of these compounds have a number of features which are different from those associated with other C_{26} limonoids occurring in the Rutaceae.[8] These include a highly oxidized C-ring and the lack of a 14,15-epoxide group. The unusual features of the proposed structure for atalantin (**1**) hinge largely on the negative results obtained by chromous chloride reduction[7,9] in attempting to show the presence of the usual 14,15-epoxide group.

This paper describes the isolation and structure determination of three limonoids from *A. monophylla*. One of these is identical with the previously reported[7] atalantin, the second with its oxidation product, dehydroatalantin, and the third limonoid, cycloepiatalantin, appears not to have been previously reported. The chemical and spectroscopic evidence obtained leads to revised structures for atalantin and dehydroatalantin.



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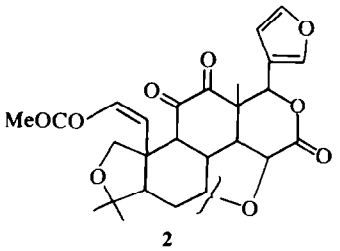

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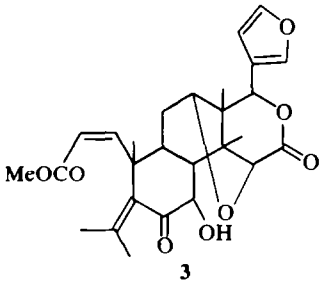

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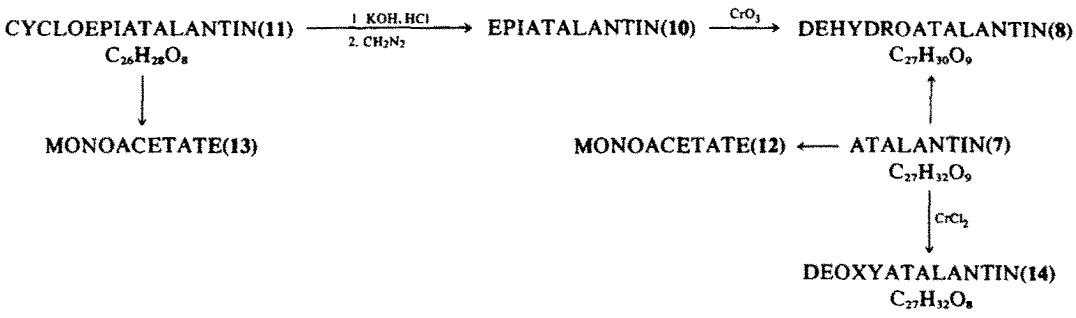
Structure

The three limonoids investigated in this study were chemically interrelated and gave analytical results as indicated in Scheme 1. All of the limonoids isolated in this study showed four C-Me resonances in their ^1H NMR spectra instead of five expected for an obacunone system. This suggests that this group of natural products belongs to the limonin (**4**) series and that C-19 has been oxidized.

It was previously known[7] that atalantin was a methyl ester of a α,β-unsaturated acid, it formed a monoacetate, and it could be oxidized to a α-diketone, dehydroatalantin, which could, in turn, be converted to a diosphenol. The acetylation and oxidation reactions have been repeated in this study. The ^1H NMR spectrum of atalantin showed typical signals[10] for a β-substituted furan ring, H-17 and H-15, the α,β-unsaturated ester system and AB doublet for H-19 of a limonoid system, as well as four C-Me resonances (Table 1). Acetylation of atalantin gave a monoacetate. The carbinol proton in atalantin (4.75 ppm) occurred at 6.09 ppm in the monoacetate, confirming the presence of a secondary alcohol group. Oxidation of the secondary alcohol group in atalantin with Jones reagent[11] resulted in the formation of dehydroatalantin, which was identical with the second limonoid isolated in this study. Dehydroatalantin was a yellow compound and its ^1H NMR spectrum (Table 1) showed many features in com-



Scheme 1. Chemical interconversions of the *Atalantia* limonoids.

Table 1. ^{1}H NMR spectra of *Atalantia* limonoids and related compounds (in ppm)[a]

Proton No.	Compound 11	13	7	12	10[b]	8	14	6[c]	5	15[d]	16[e]
α-Furan	7.42(1)	7.42(1)	7.39(1)	7.37(1)	7.38(1)	7.38(1)	7.44(1) 7.39	7.47(1)	7.43(1)	7.42(1)	7.32(1)
β-Furan	6.33(1)	6.30(1)	6.32(1)	6.32(1)	6.32(1)	6.34(1)	6.36(1)	6.41(1)	6.35(1)	6.34(1)	6.30(1)
H-17	5.58	5.58	5.49	5.44	5.55	5.41	4.94	5.46	5.48	5.48	5.37
H-19	4.01(10)	4.00(10)	4.14(10)	4.26(10)	4.21(10)	4.44(10)	3.94(10)	4.42(10)	4.30(13)	4.32(13)	—
	3.86	3.88	3.77	3.76	3.80	3.88	3.82		4.15	4.16	
H-7	3.46	4.62	4.75[f]	6.09	3.66	—	4.70	—	4.37	5.61	—
H-1	7.72(6)	7.76(6)	6.58(12)	6.57(12)	6.54(12)	6.62(12)	6.52(12)	4.49	4.37	4.38	5.45(12)
H-2	6.24(6)	6.26(6)	5.86(12)	5.86(12)	5.88(12)	5.86(12)	5.86(12)	—	2.7–2.9[g]	2.92(16) 2.66	5.67(12)
H-15	3.89	3.67	4.42	3.73	3.82	3.76	7.10	3.62	4.16	3.83	3.63
H-9	3.02	2.91	3.32	3.44	3.38	3.63	3.19	—	—	2.94	—
H-5	—	—	3.09	3.03	3.06	3.16	3.12	3.39	3.12	3.08	—
C-Methyls	1.36	1.38	1.35	1.32	1.29	1.30	1.33	1.43	1.44	1.40	1.47
	1.24	1.23	1.29	1.24	1.29	1.25	1.33	1.14	1.36	1.32	1.23
	1.20	1.17	1.22	1.21	1.15	1.20	1.19	1.14	1.21	1.27	1.20
	1.10	1.15	0.87	0.93	1.05	1.04	1.11	1.02	0.65	0.78	1.13
											1.08
Methoxy	—	—	3.67	3.70	3.72	3.62	3.67	—	—	—	3.60
Acetoxy	—	1.94	—	2.27	—	—	—	—	—	2.28	—

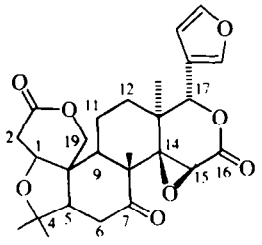
[a] Data collected in $CDCl_3$ at 100 MHz unless otherwise indicated; coupling constants in parentheses in Hz. The areas of the signals were consistent with their assignments.
[b] 60 MHz.
[c] $CDCl_3$–$(CD_3)_2SO$.
[d] Ref. 12.
[e] Ref. 10 (60 MHz).
[f] Broad.
[g] Unresolved.

mon with atalantin. Its spectroscopic properties suggested that it contained an α-diketone system.

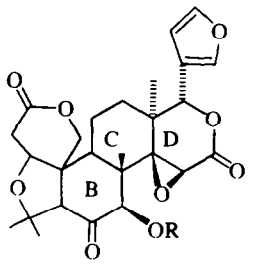
Oxidation of the 7-OH group of atalantin to give dehydroatalantin results in an upfield shift of the H-15 resonance (4.42–3.76 ppm) and a downfield shift of the upfield C-Me resonance (Table 1). This parallels a similar change of the H-15 resonance in comparing rutaevin (**5**), 4.16 ppm, to 6-ketolimonin (**6**), 3.62 ppm, as well as a downfield shift to the upfield C-Me signal in the rutaevin† series.[12] These changes in the positions of the H-15 signal with modification of the OH group in atalantin suggest that the OH group is located at the 7-position. The sensitivity of the H-15 resonance to changes of functionality at the 7-position in limonoids has been pointed out previously.[10] Since the OH group is part of an α-hydroxyketone system, the keto group can only be located at the 6-position.

This arrangement was supported by the fact that the ^{1}H NMR spectra of atalantin and dehydroatalantin both showed a one-proton singlet in the region of 3.10 ppm, which was consistent with a proton adjacent to a CO group and was assigned to H-5. Such a singlet in the same region is also discernible in the spectrum of rutaevin (**5**).[12] By means of spin decoupling experiments, the signal at 3.09 ppm in atalantin showed long range coupling with the carbinol proton of the alcohol group at 4.75 ppm. Finally, in contrast to the results of previous workers,[6] chromous chloride reduction[9] of atalantin gave deoxyatalantin, providing definitive chemical evidence for the presence of a 14,15-epoxide group. Compared to atalantin, the ^{1}H NMR spectrum of deoxyatalantin showed the expected displacement of signals for H-21, H-23, H-17 and H-15, which paralleled those exhibited by limonin and deoxylimonin. The above spectroscopic data clearly establish

†More recently, (Y. Hirose, *Chem. Pharm. Bull. Japan* **19**, 1268 (1971)) rutaevin has been formulated as 6-hydroxylimonin, but the limited evidence presented is equally consistent with structure **5**.



Limonin (**4**)



Rutaevin (**5**) R = H
Rutaevin Acetate (**15**) R = Ac

an α-hydroxyketone and α-diketone system in atalantin and dehydroatalantin respectively, and allow structures **7** and **8** to be advanced for these limonoids.

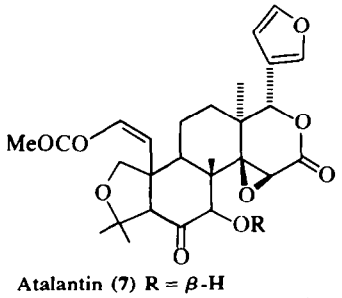
The MS of a number of limonoids have previously been reported[13] and assignments of fragments made. The fragmentation of the D-ring, 14,15 - epoxy - δ - lactone system, dominates the mass spectra of those limonoids containing this structural feature. This diagnostic fragmentation is found in MS of dehydroatalantin (**8**), which showed a very weak molecular ion. Fragmentation of the D-ring leads to abundant fragments of *m/e* 375 and 357. The mass spectra of limonin (**4**) and rutaevin (**5**)[12] show a similar fragmentation. These MS results support the presence of the usual epoxy - δ - lactone system in the *Atalantia* limonoids.

The IR spectrum of the third limonoid, cycloepiatalantin, showed a hydroxy band as well as CO bands at 1740 and 1690 cm^{-1}. The ^1H NMR spectrum of cycloepiatalantin (Table 1) showed bands assigned to (a) a β-substituted furan system,[10] (b) an AB doublet assigned to an α,β-unsaturated carbonyl system, (c) singlets for H-17 and H-15 of a typical limonoid system,[10] (d) a two-proton AB doublet assigned to H-19 and (e) a singlet for a carbinol proton of a secondary alcohol. The presence of a cyclopentenone system was consistent with the relatively small coupling constants (5.5 Hz) of the vinyl AB doublet[14] and the 1690 cm^{-1} IR band. The UV spectrum, λ_{max} 210 (ϵ 10,000), 323 (ϵ 200) nm, supported the presence of a cyclopentenone system.[15]

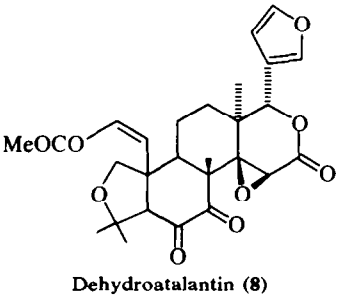
The two-proton AB system in the ^1H NMR spectrum at 4.01 and 3.86 ppm (J = 9 Hz) indicated the presence of a methylene group carrying an oxygen substituent, similar to that at C-19 in limonin. However, the relative unfield position of the signals compared to those in limonin (**4**) argues for the attachment of an ether oxygen rather than a lactone system as found in **4**. In fact, the chemical shift and coupling constant are very similar to those of the C-19 cyclic ether system in methyl limonilate (**9**).[10]

A one-proton signal at about 4 ppm, whose position was concentration-dependent, proved to be exchangable with D_2O, indicating the presence of a OH group. A possible carbinol proton was observed as a singlet at 3.46 ppm. When 10% of DMSO-d_6 was added to the $CDCl_3$ solution, the OH proton moved downfield to 6.43 ppm and became a doublet (J = 5 Hz).[16] The carbinol proton also became a doublet and was shown by double irradiation to be coupled to the OH proton. Thus, the presence of a secondary OH group is demonstrated.

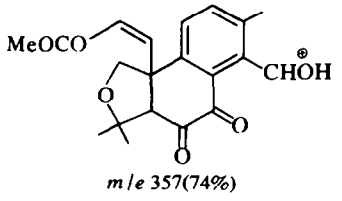
The remaining features of the spectrum were a one-proton multiplet centered at 3.02 ppm and a complex pattern integrating for four protons between 1.4 and 2.1 ppm. Double irradiation experiments showed coupling between the one-proton signal and part of the four-proton pattern. Upon addition of the shift reagent, $Eu(FOD)_3$,[17] two of the four protons moved downfield away from the other two. The faster moving pair were shown by decoupling and INDOR experiments[18] to be coupled to both the slower moving pair and the one proton multiplet. The latter was coupled only to the faster moving pair. These results are consistent with the presence of a normal



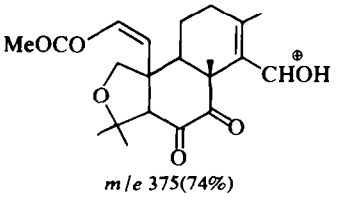
Atalantin (**7**) R = β-H
Atalantin Acetate (**12**) R = β-Ac
Epiatalantin (**10**) R = α-H



Dehydroatalantin (**8**)



m/e 357(74%)



m/e 375(74%)

unsubstituted limonoid C-ring. The one-proton signal would then be assigned to the 9-proton,† the faster moving pair to the 11α- and 11β-protons, and the other two to the 12α- and β-protons. The sum of the spectroscopic evidence to this point indicated that C- and D-rings of cycloepiatalantin were identical with those of other C_{26} limonoids occurring in the Rutaceae. However, anomalous features were clearly indicated in the vicinity of the A- and B-rings. No limonoid containing a cyclopentenone system other than in the D-ring has been isolated to date.[8] The furan, epoxylactone, cyclopentenone and hydroxyl groups accounted for six of the eight O atoms in the molecular formula. The broadness of the CO band attributed to the lactone in the IR spectrum suggested the possible presence of another CO group. This was confirmed by the ^{13}C NMR spectrum of cycloepiatalantin (see below), which indicated the presence of a second keto group. Since only three CO resonances were observed in the C-13 spectrum, the remaining O atom must be single-bonded, either as a OH or ether group.

Acetylation of cycloepiatalantin with acetic anhydride-pyridine gave a monoacetate, as shown by the appearance of a 3-proton acetate Me signal in the NMR spectrum. The carbinol resonance previously observed at 3.46 ppm in cycloepiatalantin was located at 4.62 ppm in the acetate. The IR spectrum of the monoacetate did not show an OH band. Therefore, cycloepiatalantin contains only one OH group, and the remaining oxygen is an ether function. The ether oxygen must join the carbon whose methylene protons give rise to the AB system at about 4 ppm and a completely substituted carbon, since all other proton signals have been assigned. Thus, there is a cyclopentenone system, a cyclic ether ($R–CH_2–O–CR_3$), a ketone and an OH group whose positions in the molecule remain to be assigned. The changes observed in the NMR spectrum when cycloepiatalantin was acetylated provide clues to the position of the OH group. The only significant changes, aside from that of the carbinol proton, were upfield shifts of 0.23 ppm for H-15 and 0.11 ppm for H-9 (Table 1). This would suggest the 7-position as the site of the OH group. Acetylation of 7- α-limonol caused an upfield shift for H-15 of 0.25 ppm, compared to a 0.55 ppm upfield shift in the case of 7-β-limonol (epilimonol).[10] The effect of acetylation on the 9-proton, which is α-oriented in the limonoids, is also in favor of a 7-α-OH group.

Cycloepiatalantin was inert to sodium bismuthate[19] and triphenyltetrazolium chloride,[20] suggesting the lack of an α-hydroxyketone system. Moreover, it was recovered unchanged from attempted oxidation with Jones reagent.[11] Nevertheless, cycloepiatalantin must be a secondary alcohol based on the NMR evidence described above. The contradictory results, on the whole, suggest that cycloepiatalantin has a secondary alcohol group which is not easily oxidized to the corresponding ketone. Since all the oxidation results were negative, the presence of an α-hydroxyketone system is not excluded.

Finally, treatment of cycloepiatalantin with base, acidification, and esterification with diazomethane gave a product, epiatalantin (**10**), which was not identical with atalantin but which nevertheless could be oxidized by Jones reagent[11] to dehydroatalantin (**8**). This conversion appears to involve the cleavage of a cyclic β-diketone system to give the related keto acid. In spite of the negative oxidation results, but in view of the chemical conversion of cycloepiatalantin to dehydroatalantin (**8**), an α-hydroxyketone system must also be present in cycloepiatalantin. The assembly of the structural features discussed above for cycloepiatalantin then leads to structure **11**.

Cycloepiatalantin (**11**) contains an unusual structural feature, three rings sharing a common C–C bond. Compounds of this type are known as propellanes.[21] So far as we are aware, the only other natural product containing a propellane system is the alkaloid batrachotoxin.[22]

The revision of structures for atalantin (**7**) and dehydroatalantin (**8**) suggests that on biogenetic grounds atalantolide (**3**)[6] should probably be formulated with a 14 - 15 - epoxy - δ - lactone D-ring. The C-4, C-19 ether bridge exhibited by the *Atalantia* limonoids is a feature not found in other limonoids of the Rutaceae.

Nevertheless, the structures accord well with biogenetic patterns for the C_{26} bitter principles. The oxidation level of C-19 and the occurrence of the genus *Atalantia* in the subfamily Aurantioideae fit the chemotaxonomic pattern previously outlined for limonoids of the Rutaceae.[23,‡]

Stereochemistry

Differences in the H-15 resonance in the *Atalantia* limonoids, as well as the non-identity of the initial A-ring cleavage product of cycloepiatalantin (**11**), epiatalantin (**10**), with atalantin (**7**), indicate that these compounds are epimeric at C-7. This was proven by the subsequent oxidation of both **7** and **10** to dehydroatalantin (**8**), in which the C-7 stereochemistry is destroyed. Because of their close proximity, the position of the H-15 resonance is a good indication of the stereochemistry at the 7-position. An equatorial hydroxy or acetoxy in the 7-position causes the H-15 resonance to be further downfield than the corresponding axial isomer. Further, the H-15 resonance is upfield in the acetate relative to the parent alcohol, c.f. the pairs 7-α-limonol, 7-β-limonol (epilimonol) and their acetates.[10]

An analysis of the NMR properties of the *Atalantia* limonoids suggests that these compounds have a boat B-ring. Limonin (**4**) and closely related congeners possess a chair B-ring and a boat C-ring.[24] If the OH group were axial in cycloepiatalantin (**11**) with a chair B-ring, H-7 would be in the deshielding region of the CO group at C-6. But the position of H-7 in the NMR spectrum (3.46 ppm) is too far upfield for this to be the case. If the OH group were equatorial, it would cause the H-15 resonance to fall somewhere downfield past 4.10 ppm (as in rutaevin (**5**); Table 1). Again, this is not the case, since H-15 occurs at 3.89 ppm in **11** and at 3.82 ppm in **10**. On the other hand, if the B-ring were in the boat conformation and the 7-OH were α, both H-5 and H-7 would be equatorial. The OH group would be well clear of H-15, in accord with the observed chemical shifts of H-7 and H-15. This is the only conformation which also accounts for the long range coupling between H-5 and H-7, which requires that both protons be equatorial.[25] Dreiding models also suggest that a boat B-ring relieves some distortion in the 5-membered ether ring present in the chair form. Thus, the 7-α-configuration is preferred for cycloepiatalantin (**11**) and epiatalantin (**10**). These arguments, when considered with

†H-9 occurs at 2.41 ppm in limonin (**4**) and at 2.12 ppm in obacunone (**17**). These values were obtained by using $Eu(FOD)_3$ to move H-9 downfield far enough to be identified by spin decoupling (see Table 1 for further data on H-9).

‡Compounds **7**, **8** and **11** are non-bitter. For a discussion on bitterness of limonoids see V. P. Maier, R. D. Bennett and S. Hasegawa, *Citrus Processing Science and Technology*, Vol. II, Avi, Westport, Conn., in press.

the chemical transformation of cycloepiatalantin (**11**) into dehydroatalantin (**8**), indicate a 7-β-configuration for atalantin (**7**). The position of the H-15 resonance in atalantin (**7**) at 4.42 ppm compares well with the H-15 resonances in 7-β-limonol (4.45 ppm) and rutaevin **5** (4.25 ppm) and is well removed from the H-15 resonance in 7-α-limonol (3.88 ppm).[10] Similar arguments apply to the corresponding acetate (**12**). Thus, the 7-OH group in cycloepiatalantin (**11**) is α- and is β- in atalantin (**7**).

^{13}C *NMR assignments*

The ^{13}C NMR spectra of the *Atalantia* limonoids, in comparison with those of related limonoids (Table 2), were used as a guide during the course of this work in confirming the structural proposals. The assignments were made by comparison of the completely decoupled spectra with literature values,[26] as well as by application of chemical shift rules and comparison of spectra from compound to compound. Off-resonance decoupling and selective decoupling were also used when necessary.

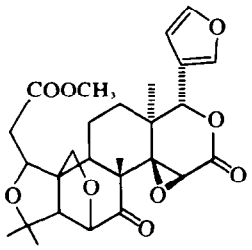
The ^{13}C NMR spectra provide independent evidence for the presence of two CO groups in cycloepiatalantin (**11**), at 201.3 and 200.3 ppm, as well as a lactone CO at 167.4 ppm. Other downfield signals at 129.8 and 169.5 ppm were assigned to the α- and β-olefinic carbons, respectively. These assignments compared well with 207 ppm for the CO and 132 and 164 ppm for the α- and β-olefinic carbons of cyclopentenone.[27] The four furan resonances completed the downfield region (Table 3). Atalantin (**7**) showed three CO resonances, but in this case one was a keto CO (209.0 ppm) and two were ester/lactone carbonyls. Two olefinic carbons assigned to an α,β-unsaturated system and the usual furan signals completed the downfield region.

The ^{13}C NMR spectrum of dehydroatalantin (**8**) showed two keto CO's (190.8 and 194.8 ppm) and two ester/lactone CO signals. The presence of an α-diketone system was confirmed by comparison of the keto resonances in **7** and **8** with the CO resonances in camphor (207.6 ppm) and the related non-enolizable α-diketone, camphorquinone (196.0 and 193.9 ppm). Assignment of the CO resonances in **8** could be made from their long-range couplings to protons.[28] C_6 should exhibit only geminal coupling (^{13}C–C–H), to H-5, while C-7 would be coupled to H-5, H-9 and the 8-Me group (vicinal, ^{13}C–C–C–H). In the undecoupled spectrum of **8** the signal at 194.6 ppm was a doublet ($J = 9$ Hz) and was therefore assigned to C-6. The other signal, at 190.6, was a broad multiplet (C-7). Two olefinic and the four furan resonances completed the downfield region of the dehydroatalantin spectrum. The positions of the resonances assigned to C-13, C-14, C-15, C-16, C-17, and the furan carbons were quite consistent from compound to compound in this series of limonoids. The consistency of these ^{13}C signals with those of known limonoids (Table 2) indicated that the C- and D-rings must be the same in this series of compounds.

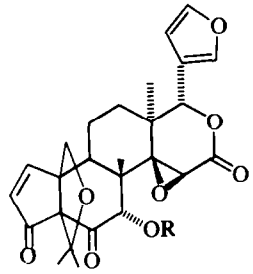
Table 2. ^{13}C NMR spectra of *Atalantia* limonoids and related compounds (in ppm)[a]

Carbon no.	Compound 11[b]	7	8	17	16	18	4[c]	19[d]
1	169.5	163.1	160.2	156.8	166.5*	82.1	78.4	156.0
2	129.8	119.9	120.3	122.7	117.9	36.0	35.6*	126.3
3	201.3*	165.9	165.5	166.7	167.3*	171.6	170.0	203.2
4	85.2	84.2	85.1	84.0	73.2	78.1	79.4	45.2
5	71.9	64.5	69.5	57.2	55.5	59.7	58.0	47.6
6	200.3*	209.0	194.6	39.9	38.0	36.0	36.0*	36.7
7	75.9	79.9	190.6	207.5	209.4	207.9	207.8	208.3
8	43.1	43.8	51.2*	52.9	52.6*	50.2	50.3	53.4
9	32.8	40.2	40.8	49.1	45.7	45.3	46.6	53.7
10	60.9	51.8	50.9*	43.1	45.1	45.3	45.2	40.0
11	16.2	19.7	21.3	17.0	16.4	17.3	17.6	17.1
12	25.5	30.8	32.5	32.6	32.0	28.0	29.0	32.1
13	37.9	38.0	37.3	37.3	37.3	38.6	37.6	37.7
14	69.3	68.3	64.9	65.1	65.5	67.6	66.7	65.7
15	56.9	52.4	52.3	53.3	53.0*	54.7	53.7	54.5
16	167.4	167.7	166.3	166.9	167.3	167.0	167.2	166.9
17	77.8	78.0	77.9	77.9	78.1	77.3	77.4	78.0
19	69.6	74.8	74.1	—	—	—	64.8	—
20	120.6	120.3	120.3	120.0	120.3	120.0	120.2	120.3
21	143.3	142.9	143.0	143.1	142.8	142.6	143.2	143.1
22	110.1	109.9	109.9	109.7	109.8	109.5	110.1	109.8
23	141.5	141.0	141.0	140.9	140.8	140.8	141.6	141.0
C-Methyls	28.8	30.8	29.0	32.0	32.6	29.2	29.6	22.0
	25.1	25.0	25.3	26.7	29.4	22.9	21.3	20.9
	17.7	20.3	19.7	21.0	20.7	19.5	19.6	20.7
	15.5	12.3	10.0	19.4	20.3	18.4	17.1	19.7
				16.4	19.4	11.8		17.4
Methoxy	—	52.4	52.3	—	51.6	51.3	—	—

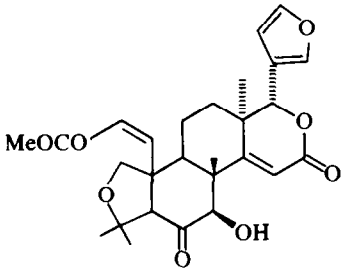
[a] In $CDCl_3$ unless otherwise indicated. Assignments of asterisked values in the same vertical column may be reversed.
[b] $CDCl_3$–$(CD_3)_2SO$.
[c] $(CD_3)_2SO$.
[d] Data from Ref. 26.



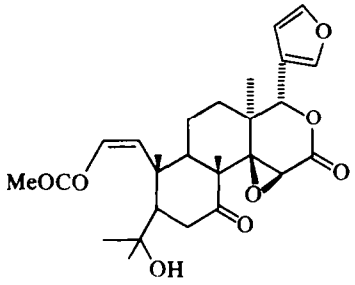
Methyl Limonilate (9)



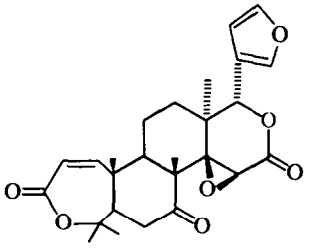
Cycloepiatalantin (11) R = H
Cycloepiatalantin Acetate (13) R = Ac



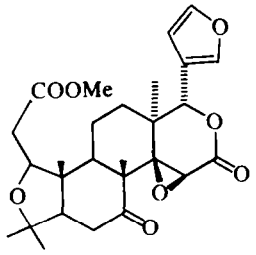
Deoxyatalantin (14)



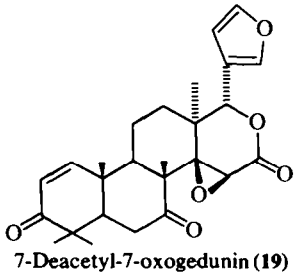
Methyl Obacunoate (16)



Obacunone (17)



Methyl Isoobacunoate (18)



7-Deacetyl-7-oxogedunin (19)

EXPERIMENTAL†

M.ps are uncorrected. ^{1}H NMR spectra were taken on a JEOL PS-100, with TMS as internal standard. ^{13}C NMR spectra were taken on a JEOL PS-100 equipped with a pulsed FT system operating at 25.15 MHz, or on a JEOL FX-60 operating at 15.00 MHz, with deuterium internal lock and TMS as internal reference. Spots on TLC plates were detected by spraying with Ehrlich's reagent and exposing to HCl gas.[29]

Atalantin (7). The powdered root bark (5 kg) of *Atalantia monophylla* collected from the Chandka forest, Orissa, was extracted with petroleum ether (60–80°). The concentrated crude extract was left in the refrigerator for 1 week, during which a dirty yellow solid separated out. It was filtered and repeatedly crystallized from MeOH in needles, m.p. 180° (Found: C, 64.70; H, 6.46. Calc. for $C_{27}H_{32}O_9$: C, 64.79; H, 6.44%).

Dehydroatalantin (8). The mother liquor of the concentrated extract was chromatographed over silica gel, and the column was washed with solvents of increasing polarity. Fractions were monitored by TLC (Silica Gel G, benzene–EtOAc, 9:1) and those giving identical spots were combined. Dehydroatalantin was eluted with benzene and was crystallised from benzene–EtOAc (1:1); m.p. 236° (Found: C, 64.94; H, 6.20. Calc. for $C_{27}H_{30}O_9$: C, 65.05; H, 6.16%).

Cycloepiatalantin (11). The defatted plant material was next extracted with chloroform and the concentrated extract was passed through a column of silica gel. On eluting with chloroform, cycloepiatalantin was isolated as glistening needles, which were crystallised from benzene–chloroform (3:1), m.p. 310° (dec), $[\alpha]_{D}^{25}$ −67.36° (chloroform). (Found: C, 67.20; H, 6.00. Calc. for $C_{26}H_{28}O_8$: C, 66.68; H, 5.98%).

Cycloepiatalantin acetate (13). To a soln of cycloepiatalantin (20 mg) in pyridine (2.5 ml) was added distilled Ac_2O (10 ml) and

†Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

the mixture was allowed to stand at room temp. for 24 hr. The mixture was then poured into crushed ice when an oily mass separated, which became semi solid on stirring. This material was filtered, washed with water, dil. HCl, and water. The dried solid was crystallised from hexane in needles, m.p. 108–110° (dec). (Found: C, 65.42; H, 5.68. Calc. for $C_{28}H_{30}O_9$: C, 65.88; H, 5.88%).

Cycloepiatalantin oxime. Cycloepiatalantin (25 mg) and hydroxylamine hydrochloride (30 mg) were dissolved in a mixture of dry pyridine (2.5 ml) and abs EtOH (2.5 ml). The mixture was refluxed for 6 hr and stirred occasionally; no precipitation occurred. The mixture was extracted with chloroform and the extract was washed with dil. HCl and water. After removal of the solvent, ether was added to the concentrated soln. The product was collected and recrystallised from benzene, m.p. 275° (dec). (Found: C, 64.18; H, 5.97; N, 2.74. Calc. for $C_{26}H_{29}O_8N$: C, 64.62; H, 6.05; N, 2.89%).

Deoxyatalantin (**14**). To a soln of 42 mg of atalantin in 2.3 ml of acetone, in a 3-ml glass-stoppered tube, was added enough aqueous chromous chloride soln (Fisher Scientific Co.) to fill the tube, which was immediately stoppered. The soln was kept at 25° for 20 hr, after which the acetone was removed in vacuum. The aqueous residue was diluted with 5 ml of H_2O and extracted with two 2-ml portions of EtOAc. The extracts were each washed with 1 ml of H_2O, combined, and evaporated, to give 35 mg of crude product, containing some unreacted atalantin. Preparative TLC (Silica Gel G, CH_2Cl_2–Et_2O, 90:10) of this material gave 14 mg of chromatographically homogeneous deoxyatalantin, which was crystallized from hexane–CH_2Cl_2; m.p. 189–191° (Found: C, 65.80; H, 6.70. Calc. for $C_{27}H_{32}O_8$: C, 66.90; H, 6.66%).

Epiatalantin (**10**). To a soln of 4 mg of cycloepiatalantin in 0.4 ml of MeOH was added 0.6 ml of 1.7 N KOH aq. After 1.5 hr at 25°, the MeOH was removed in vacuum. The aqueous residue was diluted with 1 ml of H_2O, acidified to pH 2 with 3N HCl, and extracted with two 0.5-ml portions of EtOAc. The extracts were each washed with 0.5 ml of H_2O, combined, and evaporated. The residue (3.3 mg) was dissolved in 1 ml of CH_2Cl_2 and extracted with two 0.5-ml portions of 5% $KHCO_3$ aq. The extracts were combined, acidified to pH 2 with 3N HCl, and extracted with two 0.5-ml portions of EtOAc. These extracts were each washed with 0.5 ml of H_2O, combined, and evaporated. This acidic fraction (2.4 mg) was methylated with CH_2N_2. Preparative TLC (Silica Gel G, CH_2Cl_2–Et_2O, 90:10) was then used to isolate the major component (1.5 mg). The amount obtained was too small to allow preparation of an analytically pure sample, but it gave a satisfactory Fourier-transform proton NMR spectrum.

Treatment of this compound with Jones' reagent gave a single product which was identical (TLC, NMR, IR) with **8**.

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