

Review

¹³C-NMR Data of Diterpenes Isolated from *Aristolochia* Species

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Abstract: The genus *Aristolochia*, an important source of physiologically active compounds that belong to different chemical classes, is the subject of research in numerous pharmacological and chemical studies. This genus contains a large number of terpenoid compounds, particularly diterpenes. This work presents a compilation of the ¹³C-NMR data of 57 diterpenoids described between 1981 and 2007 which were isolated from *Aristolochia* species. The compounds are arranged skeletonwise in each section, according to their structures, i.e., clerodane, labdane, and kaurane derivatives. A brief discussion on the ¹³C chemical shifts of these diterpenes is also included.

Keywords: *Aristolochia*; Aristolochiaceae; Clerodanes; Furanoditerpenes; Kauranes; Labdananes; ¹³C-NMR data.

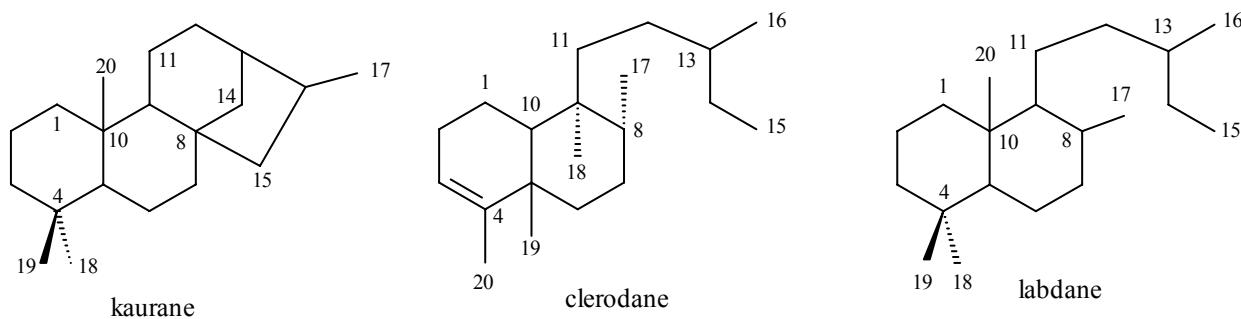
Introduction

The genus *Aristolochia* (Aristolochiaceae) consists of about 500 species mostly distributed along tropical, subtropical, and Mediterranean regions of the world [1–3]. The *Aristolochia* species are cultivated as ornamentals [4] and popularly used as sources of abortifacient, emmenagogue [5,6], sedative [7], analgesic, anticancer, anti-inflammatory, antifeedant [8], muscle relaxant [9], antihistaminic, and antiallergic [10] drugs, for intestinal worms, in the treatment of cholera, stomach ache, abdominal pain, rheumatism [11], malaria [12], wounds and skin diseases [13], and also useful in

treatment of different types of poisonous bites and stings [14,15]. Several other biological properties have been described [16]. On the other hand, consumption of many plants of the genus can lead to progressive nephrophathy and urothelial cancer in humans [17,18]. As a consequence, the distribution of herbal medicines containing *Aristolochia* extracts are prohibited in many countries due to their nephrotoxic, carcinogenic, and mutagenic properties [1].

Aristolochic acids have been frequently found in *Aristolochia* species [19]. These compounds show toxic effects at the renal level and carcinogenic properties [20,21]. Phytochemical investigations of these species revealed both the presence of aporphinic, tetrahydroprotoberberinic, benzyltetrahydroisoquinolinic, and bisbenzyltetrahydroisoquinolinic alkaloids [22] and other nitrogenated derivatives (phenantrenoids, aristolactams, and porphyrins) [23-25]. Quinones, coumarins, flavanoids, lignoids (phenylpropanoids, neolignans, and lignans), and fatty acids are frequently isolated from plants of the genus [26]. However, the most prominent compounds in *Aristolochia* are terpenoids, constituents of the essential oils isolated from the plant species. The majority of the identified terpenoids are kaurane, clerodane, and labdane diterpene derivatives (Figure 1).

Figure 1. Diterpene classes present in *Aristolochia* species.



The review “Terpenoids of *Aristolochia* and their biological activities”, which covered the literature up to 2003, lists 52 diterpenoids isolated from the genus and their pharmacological properties [16]. In the present review a new comprehensive coverage of diterpenes isolated from *Aristolochia* species up to this moment (Tables 1 to 3) is described, broadly covering 26 kauranes (Figures 2 and 3), 29 clerodanes (Figures 4 and 5), one furanoditerpene derivative (Figure 6), and 9 labdanes (Figure 7). Moreover, the ^{13}C -NMR data of these compounds are also compiled (Tables 4 and 5). For some structures no ^{13}C -NMR data was found in the investigated literature and there is disagreement concerning the ^{13}C -NMR data of ($-$)-11-hydroxykaur-16-en-19-oic acid. Sometimes different structures were given the same names.

Kaurane derivates isolated from *Aristolochia* species

Kaurane diterpenoids show several biological properties such as antioxidative, antityrosinase [27], abortifacient, and anti-inflammatory activities, they are used against snake bite poisoning [28], and present cytotoxicity against tumor cells of human prostate, colon, and breast cancer [29]. Table 1 lists the kaurane derivates isolated from *Aristolochia* species (**1** to **26** in Figures 2 and 3) and their

respective plant sources. Acetonide **13** and kaurane derivative **14** were isolated from *A. rodriquesii* and *A. triangularis*, respectively. Both compounds were also prepared from **3** [30].

Table 1. Kaurane diterpenoids isolated from *Aristolochia* species.

Clerodane	Species
<i>ent</i> -Kauran-16 β -ol [(-)-kauranol] (1)	<i>A. rodriquesii</i> [28]
<i>ent</i> -16 β (H)-Kauran-17-oic acid (2)	<i>A. elegans</i> [7]; <i>A. triangularis</i> [13]
<i>ent</i> -Kauran-16 β ,17-diol (3)	<i>A. elegans</i> [7]; <i>A. pubescens</i> [31]; <i>A. triangularis</i> [13]
<i>ent</i> -16 β (H)-Kaurane (4)	<i>A. elegans</i> [7]; <i>A. triangularis</i> [13]
<i>ent</i> -16 α (H)-Kauran-17-al (5)	<i>A. elegans</i> [7]
<i>ent</i> -Kauran-16 β ,19-diol [<i>ent</i> -16 β ,19-dihydroxykaurane] (6)	<i>A. rodriquesii</i> [28]
<i>ent</i> -16 α -Hydroxy-kauran-19-al [16 α -hydroxy-(-)-kauran-19-al] (7)	<i>A. rodriquesii</i> [28]; <i>A. triangularis</i> [32]
<i>ent</i> -16 β ,17-Dihydroxy-(-)-kauran-19-oic acid (8)	<i>A. rodriquesii</i> [28]
<i>ent</i> -16 β -Hydroxy-kauran-18-al [(-)-kauran-16 α -hydroxy-18-al] (9)	<i>A. triangularis</i> [26]
<i>ent</i> -16 β ,17-Epoxykaurane (10)	<i>A. elegans</i> [7]; <i>A. triangularis</i> [32]
<i>ent</i> -15 β ,16 β -Epoxy-17-hydroxy-kauran-19-oic acid (11)	<i>A. rodriquesii</i> [28]
<i>ent</i> -15 β ,16 β -Epoxykauran-17-ol (12)	<i>A. triangularis</i> [13]
<i>ent</i> -16 β ,17-Isopropylidenedioxy-(-)-19-oic acid (13)	<i>A. rodriquesii</i> [28]
17-nor-(-)-Kauran-16-one (14)	<i>A. triangularis</i> [13]
<i>ent</i> -17-Hydroxy-kaur-15-en-19-oic acid (15)	<i>A. rodriquesii</i> [28]
<i>ent</i> -Kaur-15-en-17-ol (16)	<i>A. elegans</i> [7]; <i>A. pubescens</i> [31]; <i>A. triangularis</i> [13,32]
<i>ent</i> -11 β -Hydroxy-kaur-16-en-19-oic acid [(-)-11-hydroxy-kaur-16-en-19-oic acid] (17)	<i>A. anguicida</i> [33]
<i>ent</i> -Kaur-16-en-19-oic acid [kaurenic acid] (18)	<i>A. anguicida</i> [33]; <i>A. rodriquesii</i> [28]; <i>A. triangularis</i> [13]
(-)- <i>ent</i> -Kaur-16-ene (19)	<i>A. triangularis</i> [13,32]
(-)- <i>ent</i> -Kaur-16-en-19-ol (20)	<i>A. triangularis</i> [13,32]
(-)- <i>ent</i> -Kaur-16-en-19-al (21)	<i>A. triangularis</i> [13,32]
<i>ent</i> -7 β -Hydroxy-kaur-16-en-19-oic acid (22)	<i>A. anguicida</i> [34]
<i>ent</i> -Kaur-16-en-3 β ,19-diol [<i>ent</i> -3 β ,18-dihydroxykaur-16-ene] (23)	<i>A. rodriquesii</i> [28]
<i>ent</i> -16 β -Hydroxy-17-kauranyl aristolachate I [aristoloin I] (24)	<i>A. elegans</i> [4]
<i>ent</i> -16 β -Hydroxy-17-kauranyl aristolachate II [aristoloin II] (25)	<i>A. pubescens</i> [31]
<i>ent</i> -17-Hydroxy-16 β -kauranyl aristolachate I [aristolin] (26)	<i>A. elegans</i> [4]

Usual names are given in brackets

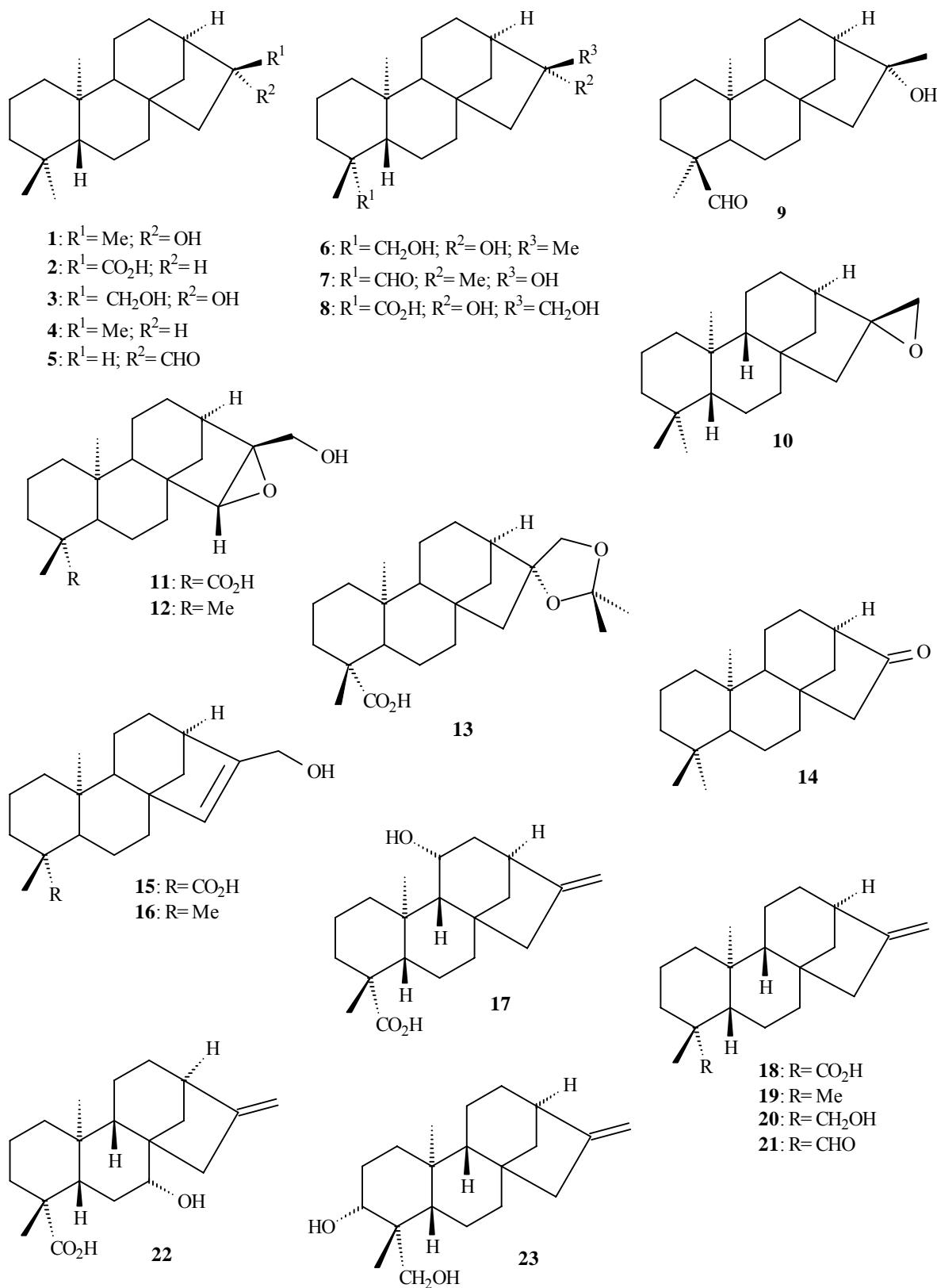
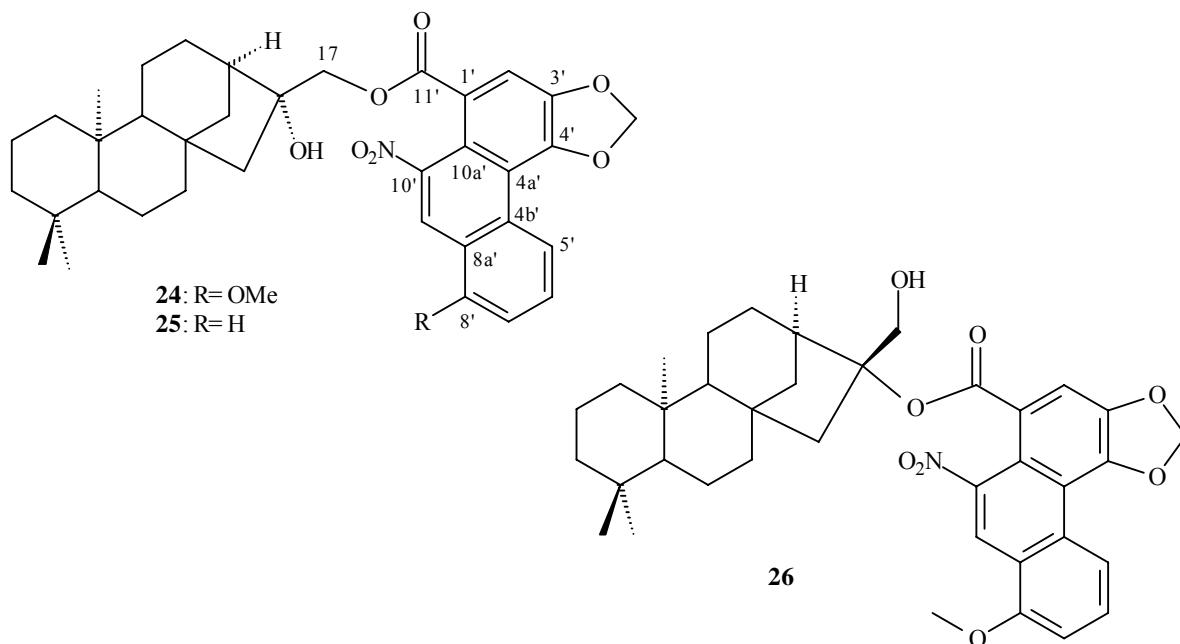
Figure 2. Kaurane diterpenoids isolated from *Aristolochia* species.

Figure 3. Substituted kaurane diterpenoids isolated from *Aristolochia* species.

Clerodane derivatives isolated from *Aristolochia* species

Clerodane diterpenoids show a broad spectrum of biological properties [35,36] including insecticidal activity [37]. Table 2 shows the clerodane diterpenoids isolated from the genus *Aristolochia* (**27** to **55** in Figures 4 and 5) and their respective plant sources. Structure **52** has been also named as 2-oxokolavenic acid (**50**). The corresponding acid of **49** has been described by Wu *et al.* [16].

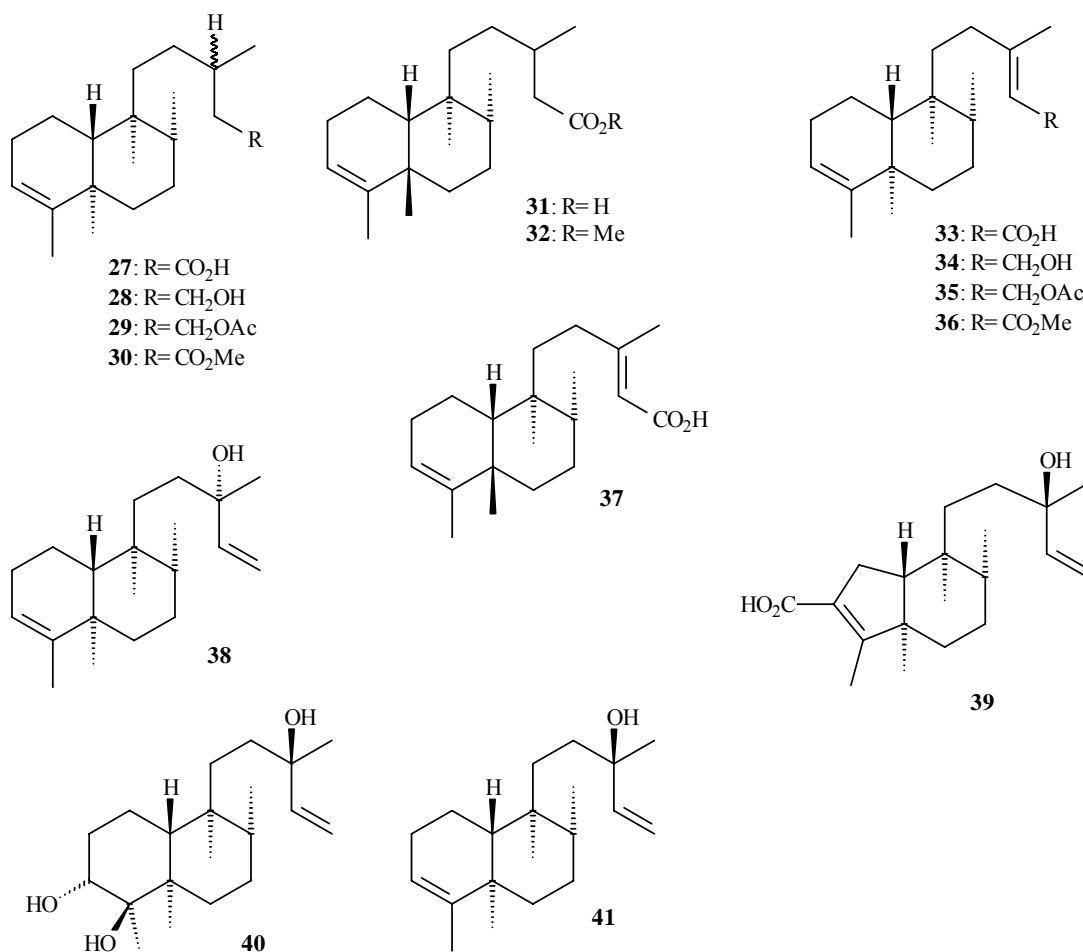
Table 2. Clerodane diterpenoids isolated from *Aristolochia* species.

Clerodane	Species
(5R,8R,9S,10R)- <i>ent</i> -3-Cleroden-15-oic acid [13,14-dihydrokolavenic acid; populifolic acid] (27)	<i>A. brasilienses</i> [38]; <i>A. cymbifera</i> [39]; <i>A. galeata</i> [40]
(5R,8R,9S,10R)- <i>ent</i> -3-Cleroden-15-ol [dihydrokolavenol] (28)	<i>A. galeata</i> [40]
(5R,8R,9S,10R)- <i>ent</i> -15-Ethanoyl-3-clerodene [dihydrokolavenol acetate] (29)	<i>A. galeata</i> [40]
Methyl (5R,8R,9S,10R)- <i>ent</i> -3-cleroden-15-oate [methyl populifoloate]) (30)	<i>A. esperanzae</i> [38]; <i>A. galeata</i> [40]
(5S,8R,9S,10R)- <i>ent</i> -3-Cleroden-15-oic acid [<i>epi</i> -populifolic acid] (31)	<i>A. cymbifera</i> [39]
Methyl (5S,8R,9S,10R)- <i>ent</i> -3-cleroden-15-oate (32)	<i>A. cymbifera</i> [39]
(5R,8R,9S,10R)- <i>ent</i> -Clerod-3,13-dien-15-oic acid [$\Delta^{13,14}$ -kolavenic acid] (33)	<i>A. brasilienses</i> [38]; <i>A. galeata</i> [40]
(5R,8R,9S,10R)- <i>ent</i> -Clerod-3,13-dien-15-ol [$\Delta^{13,14}$ -kolavenol] (34)	<i>A. galeata</i> [40]
(5R,8R,9S,10R)- <i>ent</i> -15-Ethanoyl-clerod-3,13-diene [acetyl kolavenoate] (35)	<i>A. galeata</i> [40]
Methyl (5R,8R,9S,10R)- <i>ent</i> -clerod-3,13-dien-15-oate [methyl kolavenoate] (36)	<i>A. esperanzae</i> [38]; <i>A. galeata</i> [40]

Table 2. Cont.

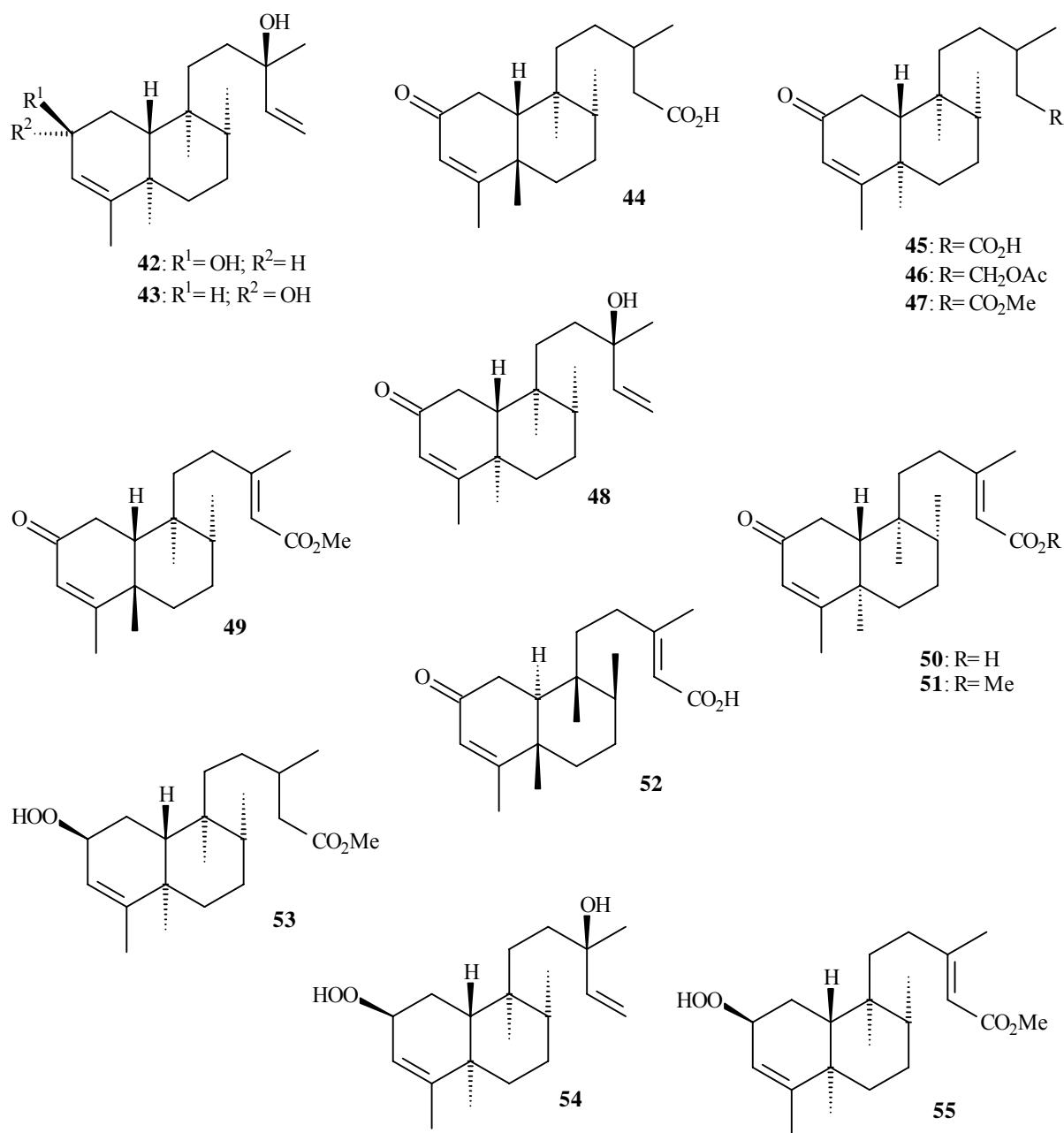
Clerodane	Species
(5S,8R,9S,10R)- <i>ent</i> -Clerod-3,13-dien-15-oic acid (37)	<i>A. brasilienses</i> [38]
(5R,8R,9S,10R)- <i>ent</i> -Clerod-3,14-dien-13 β -ol [(+)-kolavelool] (38)	<i>A. galeata</i> [40]
(5R,8R,9S,10R)-(4 \rightarrow 2)- <i>abeo</i> -Clerod-13 β -hydroxy-2,14-dien-3-oic acid [(+)-(4 \rightarrow 2)- <i>abeo</i> -kolavelool-3-oic acid] (39)	<i>A. chamissonis</i> [41]
(5R,8R,9S,10R)- <i>ent</i> -Clerod-14-en-3 β ,4 α ,13 α -triol [(-)-3 α ,4 β -dihydroxykolavelool] (40)	<i>A. chamissonis</i> [41]
(5R,8R,9S,10R)- <i>ent</i> -Clerod-3,14-dien-13 α -ol [(-)-kolavelool] (41)	<i>A. chamissonis</i> [41]; <i>A. cymbifera</i> [38]; <i>A. galeata</i> [38]
(5R,8R,9S,10R)- <i>ent</i> -Clerod-3,14-dien-2 α ,13 α -diol [(-)-2 β -hydroxykolavelool] (42)	<i>A. chamissonis</i> [41]
(5R,8R,9S,10R)- <i>ent</i> -Clerod-3,14-dien-2 β ,13 α -diol [(+)-13- <i>epi</i> -2 α -hydroxykolavelool; 13- <i>epi</i> -roseostachenol] (43)	<i>A. chamissonis</i> [41]
(5S,8R,9S,10R)-2-Oxo- <i>ent</i> -3-cleroden-15-oic acid (44)	<i>A. brasilienses</i> [38]
(5R,8R,9S,10R)-2-Oxo- <i>ent</i> -3-cleroden-15-oic acid [2-oxopopulifolic acid] (45)	<i>A. brasilienses</i> [39]; <i>A. cymbifera</i> [39]; <i>A. galeata</i> [40]
(5R,8R,9S,10R)-2-Oxo- <i>ent</i> -15-ethanoyl-3-clerodene [2-oxodihydrokolavenol acetate] (46)	<i>A. galeata</i> [40]
Methyl (5R,8R,9S,10R)-2-oxo- <i>ent</i> -3-cleroden-15-oate [methyl 2-oxopopulifolate] (47)	<i>A. esperanzae</i> [38]
(5R,8R,9S,10R)-2-Oxo- <i>ent</i> -clerod-3,14-dien-13 α -ol [(-)-13- <i>epi</i> -2-oxokolavelool; 13- <i>epi</i> -roseostachenone] (48)	<i>A. chamissonis</i> [41]
Methyl (5S,8R,9S,10R)-2-oxo- <i>ent</i> -clerod-3,13-dien-15-oate (49)	<i>A. brasilienses</i> [38]
(5R,8R,9S,10R)-2-Oxo- <i>ent</i> -clerod-3,13-dien-15-oic acid [$\Delta^{13,14}$ -2-oxokolavenic acid] (50)	<i>A. brasilienses</i> [38]
Methyl (5R,8R,9S,10R)-2-oxo- <i>ent</i> -clerod-3,13-dien-15-oate [methyl $\Delta^{13,14}$ -2-oxokolavenoate] (51)	<i>A. esperanzae</i> [38]
(5S,8S,9R,10S)-2-Oxo- <i>ent</i> -clerod-3,13-dien-15-oic acid (52)	<i>A. brasilienses</i> [38]
Methyl (5R,8R,9S,10R)- <i>ent</i> -2 α -hydroperoxy-3-cleroden-15-oate (53)	<i>A. esperanzae</i> [38]
(5R,8R,9S,10R)- <i>ent</i> -2 α -Hydroperoxy-clerod-3,14-dien-13 α -ol [(-)-2 β -hydroperoxykolavelool] (54)	<i>A. chamissonis</i> [41]
Methyl (5R,8R,9S,10R)- <i>ent</i> -2 α -hydroperoxy-clerod-3,13-dien-15-oate (55)	<i>A. esperanzae</i> [38]

Usual names are given in brackets

Figure 4. Clerodane diterpenoids isolated from *Aristolochia* species.

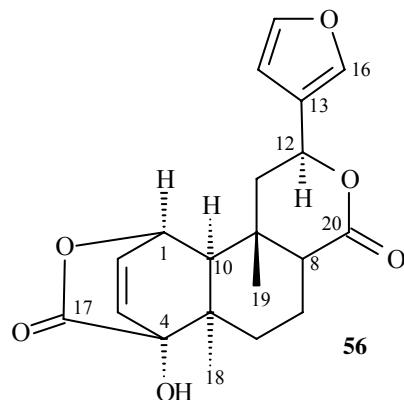
Furanoditerpene isolated from *Aristolochia* species

Analgesic and anti-inflammatory activities have been observed for furanoditerpenes [42,43], and their derivatives also show sedative [42], anticonvulsant [44], and plant growth regulatory activities [45]. Columbin (**56**) was isolated from *A. albida* [46] (Figure 6). The furan moiety is not fused to other rings, as is commonly found in several furanoditerpenes from natural products or synthesized [47]. It is the only furanoditerpene found in the genus *Aristolochia*.

Figure 5. Clerodane diterpenoids isolated from *Aristolochia* species, showing oxygenated C-2.

Labdane derivatives isolated from *Aristolochia* species

Labdane diterpenoids are fungal growth regulator and plant growth inhibitor [48-50], showing high antibacterial activity [51]. Commercially, labdanes are used as natural fixatives, modifiers, and lotions by the perfume industry, and as a flavouring agent in the tobacco industry [52]. Table 3 shows the labdane diterpenoids isolated from *Aristolochia* species (**57** to **67** in Figure 7). Structures **58** and **59** have both been named as *ent*-labd-13-en-8 β -ol-15-oic acid [53].

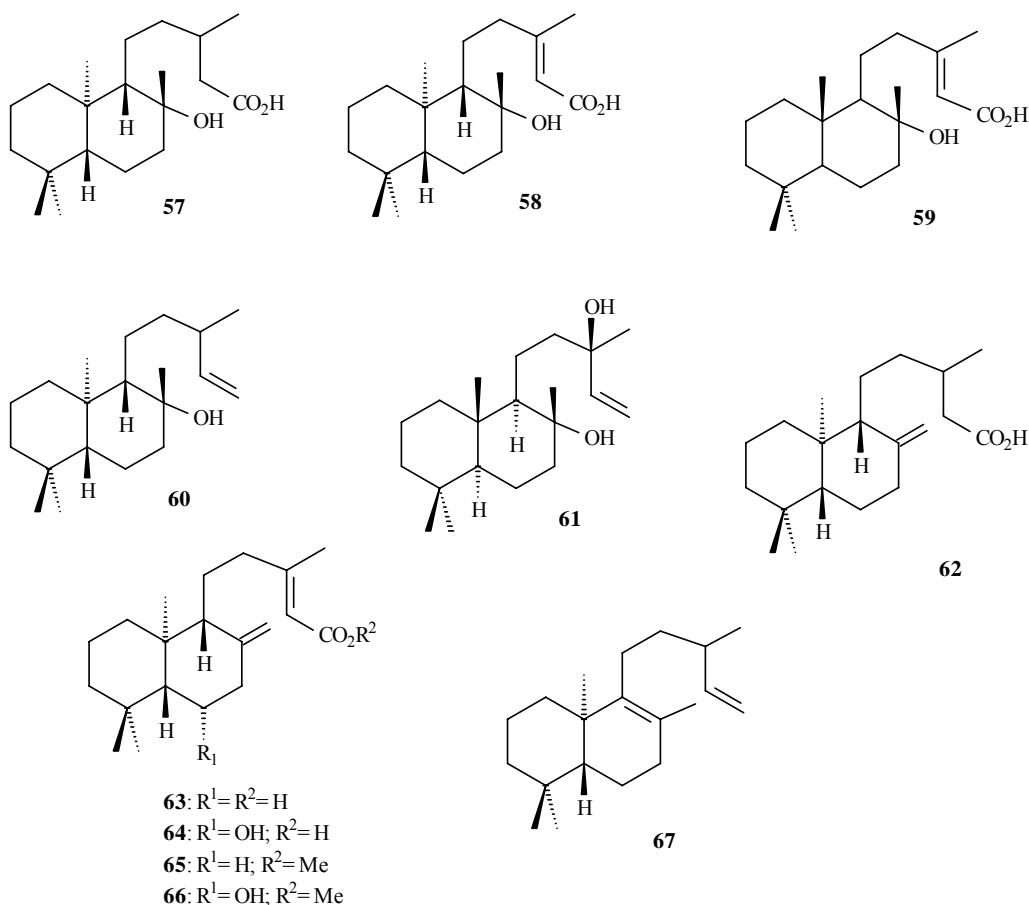
Figure 6. Furanoditerpene isolated from *Aristolochia* species.**Table 3.** Labdane diterpenoids isolated from *Aristolochia* species.

Clerodane	Species
(5R,8R,9S,10S)- <i>ent</i> -Labdan-8 β -hydroxy-15-oic acid (57)	<i>A. galeata</i> [40]
(5R,8R,9S,10S)- <i>ent</i> -Labd-13-en-8 β -hydroxy-15-oic acid	<i>A. galeata</i> [40]
[$\Delta^{13,14}$ - <i>ent</i> -labd-8 β -ol-15-oic acid] (58)	
(5R,8R,9S,10S)- <i>ent</i> -Labd-14-en-8 β -ol (60)	<i>A. cymbifera</i> [40]
(5S,8R,9R,10R)- <i>ent</i> -Labd-14-en-8 β ,13 α -diol (61)	not isolated from <i>Aristolochia</i> species [54]
(5R,9S,10S)- <i>ent</i> -Labd-8(17)-en-15-oic acid (62)	<i>A. ringens</i> [55]
(5R,9S,10S)- <i>ent</i> -Labd-8(17),13-dien-15-oic acid [copalic acid] (63)	<i>A. esperanzae</i> [40]; <i>A. galeata</i> [40]
(5R,9S,10S)- <i>ent</i> -Labd-6 β -hydroxy-8(17),13-dien-15-oic acid (64)	<i>A. esperanzae</i> [40]
Methyl (5R,8R,9S,10S)- <i>ent</i> -labd-8(17),13-dien-15-oate [methyl copalate] (65)	<i>A. esperanzae</i> [40]
Methyl (5R,9S,10S)- <i>ent</i> -labd-6 β -hydroxy-8(17),13-dien-15-oate (66)	<i>A. esperanzae</i> [40]
(5R,10S)- <i>ent</i> -Labd-8,14-diene (67)	<i>A. cymbifera</i> [40]

Usual names are given in brackets

¹³C-NMR data of diterpenes

Tables 4 and 5 show the ¹³C-NMR data of the diterpenoids **1** to **67**. In Table 4 the ¹³C-NMR data of **17** (in CDCl₃) were reassigned and a new structure **22** was proposed according to ¹³C-NMR data in CDCl₃, C₅D₅N, and DMSO-*d*₆ [34] (see Figure 2). The carbon chemical shifts of the kaurane diterpenoids **1** to **23** are characteristic only at region between δ_{C} 38.0 and 42.0 assigned to C-1 and C-10. The other carbon chemical shifts do not show any characteristic features for this skeleton type. In diterpenes **15** and **16** containing a double bond between C-15 and C-16, the carbon chemical shifts are registered near δ_{C} 135.0 and 145.0, respectively. On the other hand, the double bond is located between C-16 and C-17 of **17** to **23** and their carbon chemical shifts are registered near δ_{C} 156.0 and 103.0, respectively.

Figure 7. Labdane diterpenoids isolated from *Aristolochia* species.**Table 4.** ^{13}C -NMR data (in CDCl_3) of diterpenes from *Aristolochia* species.

Carbon	Compound / δ_{C} (in ppm)														
	1 [56]	2 [13]	3 [31]	4 [13]	6 [28]	8 [57,58]	10 [59]	11 [28]	12 [13]	13 [28]	14 [56]	15 [28]	16 [13]	17 [33]	18 [33]
1	42.0	39.2	40.3	40.9	40.35	41.1	40.4	39.82	40.4	40.66	41.0	40.73	42.0	39.10	41.13
2	18.6	18.2	18.6	18.6	17.97 ^a	19.8	18.6	18.39 ^a	18.7	19.06	18.5	19.05 ^a	18.6	20.07	19.52
3	42.0	42.0	41.9	42.0	35.55	38.7	42.0	34.33	42.1	38.39	41.9	38.03	43.8	35.00	38.23
4	33.2	33.1	33.2	33.6	38.50	43.9	33.2	48.47	33.3	43.66	33.2	43.55	33.2	43.60	44.66
5	56.2	56.1 ^a	56.2	56.1 ^a	56.90 ^b	57.0	56.2	56.68 ^b	55.9	56.96	56.1	56.65	55.8	49.80	57.49
6	20.4	20.6	20.4	20.7	20.49	23.0	20.2	20.10	19.3	22.00	19.2	20.70	19.2	19.51	22.28
7	40.3	40.3	42.0	40.4	42.31	42.8	41.1	42.02	32.5	41.52	40.3	39.24	39.2	40.84	41.71
8	45.3	45.3	44.7	45.1	45.17	45.0	45.4	45.20	43.4	44.51	42.5	48.81	48.8	47.63	44.17
9	56.8	56.0 ^a	56.7	56.0 ^a	56.70 ^b	56.3	55.9	55.20 ^b	50.8	55.40	55.0	47.57	48.3	47.89	55.55
10	39.3	38.0	39.4	39.2	39.15	40.1	39.3	39.44	39.2	39.64	39.4	39.72	39.4	40.00	40.09
11	18.0	18.5	18.3	18.3	17.93 ^a	19.0	19.3	18.13 ^a	18.2	19.06	18.5	18.75 ^a	18.6	77.52	18.43
12	26.9	31.2	26.3	31.3	26.06	26.8	29.2	26.90	27.0	27.06	29.7	25.31	25.6	33.97	33.53
13	49.0	44.7	45.5	41.4	48.64	45.9	42.7	48.93	36.0	45.64	47.9	40.92	41.1	44.41	44.28
14	37.7	40.8	37.3	38.1	37.36	37.8	38.6	37.81	36.0	37.88	37.5	43.71	40.4	39.79	40.13
15	58.0	45.0	53.4	44.7	57.66	53.9	48.9	57.80	65.7	55.54	55.2	135.39	135.7	47.41	49.39
16	79.4	55.9	81.9	45.9	79.16	81.7	66.4	79.29	69.5	89.16	222.5	145.82	145.6	155.24	156.32

Table 4. Cont.

17	24.5	182.5	66.4	14.8	24.05	66.5	50.4	24.47 ^c	59.9	70.05	-	60.63	61.1	104.09	103.69
18	33.5	33.5	33.5	33.2	26.89	29.3	33.6	24.26 ^c	33.6	28.93	33.6	28.87	35.5	30.08	29.38
19	21.6	21.5	21.5	21.6	64.98	180.1	21.6	205.80	21.6	182.64	21.7	180.90	21.5	184.05	184.00
20	18.0	17.3	17.8	17.4	18.11	16.0	17.8	16.40	17.5	15.74	18.0	15.25	17.6	15.93	16.02
1'												108.39			
2'												26.81			
3'												26.91			
Compound / δ_{C} (in ppm)															
Carbon	19 [56]	20 [57] ^(?)	22 [34]	22 [34] ^(P)	22 [34] ^(D)	23 [60]	27 [26]	27 [34]	29 [61]	30 [38]	30 [38]	31 [39]	32 [39]	33 [38]	33 [39]
1	41.3	40.5	39.79	40.9	40.3	38.7	18.3	17.4	17.3	17.5	18.2	17.7	17.6	17.3	18.3
2	18.7	18.3	20.07	19.7	19.0	27.6	26.8	27.6	27.5	27.1	26.8	24.1	24.0	27.5	26.9
3	42.0	35.7	40.84	38.5	37.9	80.6	120.5	120.6	120.4	120.0	120.4	123.2	123.1	120.5	120.4
4	33.3	39.3	43.60	43.7	42.5	42.7	144.5	144.4	144.4	143.7	144.4	139.9	139.9	144.5	144.4
5	56.1	56.9	49.80	49.5	46.3	55.8	38.2	38.3 ^a	38.3	38.0 ^a	38.4	38.5	38.2	38.3 ^a	38.2
6	20.3	20.5	35.00	30.4	29.3	20.1	36.9	36.5	35.9	36.4	36.8	37.8	37.7	36.4 ^b	36.8
7	40.4	41.7	77.52	76.2	75.0	41.3	27.6	27.0	26.8	26.4	27.5	28.8	28.7	26.9	27.5
8	44.2	44.0	47.63	48.9	48.0	43.9	36.2	36.3	36.1	36.0	36.1	37.3	37.2	36.4 ^b	36.3
9	56.1	56.2	47.89	47.4	48.6	55.8	40.0	38.7 ^a	38.1	38.3 ^a	39.9	39.9	39.9	38.4 ^a	38.3
10	39.3	38.7	40.00	39.5	38.8	39.6	46.4	46.6	46.4	46.1	46.3	44.5	44.5	46.6	46.5
11	18.1	18.2	19.51	18.5	17.7	18.3	35.5	35.1 ^b	35.5	35.0 ^b	35.4	35.1	35.0	35.0	36.3
12	33.3	33.2	33.97	34.0	33.3	33.0	29.5	35.6 ^b	35.4	35.8 ^b	29.4	29.4	29.3	36.9 ^a	35.0
13	44.2	44.2	44.41	44.3	43.4	43.9	30.9	31.0	30.6	30.6	31.0	30.9	31.1	164.4	164.6
14	39.9	39.7	39.10	39.1	38.4	38.5	41.6	41.7	36.5	41.0	41.5	41.6	41.5	114.9	114.8
15	49.2	49.1	47.41	46.6	45.6	48.8	179.4	179.8	62.8	172.8	173.8	179.4	173.8	172.0	172.1
16	156.0	155.9	155.24	156.2	155.4	155.4	19.9	19.9	19.6	19.5	19.9	19.8	19.5	19.5	19.5
17	102.8	103.0	104.09	103.6	103.2	103.1	16.0	16.1	15.7	15.5	15.9	16.0	15.9	15.9	16.0
18	33.7	27.1	30.08	28.6	28.5	22.8	19.9	18.4	18.3	18.0	19.9	33.0	33.0	18.3	20.0
19	21.7	65.6	184.05	178.2	179.0	64.3	18.0	20.0	19.3	19.5	18.0	20.1	19.9	20.0	18.0
20	17.6	18.1	15.93	15.7	15.4	18.3	18.5	18.1	17.8	17.8	18.4	17.4	17.3	17.9	18.3
C=O												178.6			
MeCO												20.8			
OMe												50.6	51.3	51.3	
Compound / δ_{C} (in ppm)															
Carbon	34 [62]	35 [63]	36 [38]	37 [38]	38 [40]	39 [41]	40 [41]	41 [41]	42 [41]	43 [41]	44 [38]	45 [40]	46 [40]	47 [38]	48 [41]
1	18.37	18.40	17.5	18.6	18.1	29.4	16.2	18.2	27.3 ^a	28.9	35.1 ^a	35.6	35.6	35.6 ^a	34.3 ^a
2	26.98	26.92	27.1	24.1	27.7	125.6	30.3	27.4	65.6	69.5	199.1	201.2	200.2	200.0	200.5
3	120.52	120.46	120.0	123.3	120.3	171.0	76.2	120.4	122.1	124.4	128.5	125.5	125.5	125.5	127.4
4	144.60	144.50	143.7	139.8	144.4	168.7	76.5	144.5	150.1	147.9	168.6	173.4	171.0	172.6	172.6
5	38.28	38.30	38.0 ^a	37.9	38.3	50.6	38.3	38.1	38.0	38.0	38.6 ^c	40.0	38.8	39.9 ^b	39.7
6	36.94	36.99	36.4	37.6 ^a	36.1	34.4	32.4	36.8	36.4	36.5	36.8 ^b	36.0	35.5	34.8 ^a	35.5
7	27.61	27.63	26.4	28.9	26.8	28.3	26.4	26.8	27.2 ^a	27.2	29.0	27.0	26.9	26.9	26.8
8	36.36	36.41	36.0	37.5	36.8	37.1	36.0	36.1	36.3	35.9	37.3	36.1	36.1	35.8	

Table 4. Cont.

9	38.72	38.72	38.3 ^a	38.9	38.1	37.5	41.2	38.3	38.9	38.6	39.3 ^c	38.6	38.6	38.8 ^b	38.3
10	46.53	46.60	46.0	44.9	46.3	53.9	40.7	46.3	40.4	45.2	45.7	45.7	45.7	45.6	45.5
11	36.63	36.72	34.2	35.0	31.8	33.5	32.2	31.8	31.0	31.8	35.4 ^a	34.9	34.9	34.9 ^a	31.1
12	32.95	32.97	37.7	37.0 ^a	35.2	35.5	35.4	35.3	36.4	35.2	36.2 ^b	36.0	34.7	35.9 ^a	34.7 ^a
13	140.93	143.22	160.8	164.5	73.3	73.0	73.5	73.4	73.2	73.3	30.7	30.8	30.4	30.9	73.0
14	123.13	118.03	114.5	115.1	145.2	144.9	145.0	145.1	146.4	145.0	41.4	41.5	36.9	41.3	144.8
15	59.51	61.44	166.5	172.4	111.6	111.9	111.6	111.8	110.9	111.9	178.7	178.9	63.0	173.4	111.9
16	16.52	16.70	18.5	19.6	27.4	27.8	27.4	27.7	26.3	27.7	19.9	19.9	19.8	19.8	27.7
17	16.07	15.98	15.5	16.1	15.8	15.0	15.9	15.9	15.8	15.9	16.0	15.7	15.8	15.7	15.6
18	18.45	17.92	18.0	20.0	18.3	11.7	21.3	18.0	17.9	17.7	20.5	18.4	18.5	18.4	18.9 ^b
19	20.03	19.99	19.5	33.2	19.8	16.9	17.2	19.8	18.3	19.9	32.1	18.9	18.7	18.9	18.2 ^b
20	18.07	18.34	17.8	17.9	17.8	18.2	18.5	18.4	18.3	18.5	18.0	17.9	18.0	18.0	17.9
C=O		170.94												178.9	
MeCO		20.94												20.8	
OMe		50.1												51.4	
	Compound / δ_{C} (in ppm)														
Carbon	49	50	51	54	56	57	58	60	61	62	63	65 (?)	66	67	
	[38]	[38]	[38]	[41]	[46]	[40]	[64]	[40]	[54] ^A	[55]	[65]	[66]	[40]	[40]	
1	35.4 ^a	35.4 ^a	35.6 ^a	22.0	74.18	39.1	39.8	39.0	40.4	33.1	39.1	19.45	43.9	36.9	
2	200.3	200.0	200.2	79.2	128.68	18.2	-	18.2	19.0	21.7	19.4	22.36	19.5	19.0	
3	128.5	125.3	125.4	116.7	136.84	42.1	41.9	41.9	42.7	35.4	42.1	24.51	42.0	41.2	
4	167.5	172.3	172.7	155.0	80.48	33.1	-	33.3	33.7	39.1	33.6	33.64	34.5	33.2	
5	38.6 ^b	39.8 ^b	39.9 ^b	37.8	37.16	55.9	56.1	55.8	56.9	36.6	55.5	55.59	57.5	51.8	
6	36.7 ^a	34.8 ^a	34.9 ^a	33.2	25.59	18.1	23.5	18.1	21.1	28.6	24.5	32.75	69.4	19.0	
7	28.9	26.7	26.9	27.1	17.33	41.3	44.7	40.5	45.1	37.4	38.3	38.41	47.7	33.5	
8	36.6	36.1	36.1	36.4	47.58	73.3	74.4	73.3	73.9	160.6	148.3	148.17	144.0	125.4	
9	39.9 ^b	38.7	38.7 ^b	39.1	35.28	59.3	61.3	58.2	62.3	48.6	56.2	57.20	56.7	140.4	
10	45.7	45.6	45.8	40.4	44.49	38.9	39.2	38.8	39.8	40.0	39.7	39.80	40.9	37.2	
11	34.0	34.2 ^a	34.0 ^a	30.7	41.90	22.3	20.5	22.4	20.0	27.5	21.5	38.96	21.6	25.3	
12	36.8 ^a	35.9 ^a	35.9 ^a	36.1	70.66	42.1	44.5	41.9	46.2	29.8	40.1	42.21	39.5	41.7	
13	160.3	162.6	160.3	73.9	124.79	30.9	163.9	30.9	73.3	30.8	164.3	160.69	160.7	31.1	
14	115.2	115.1	115.3	146.3	108.40	40.5	114.7	144.7	147.5	41.4	114.6	115.73	115.2	145.9	
15	167.0	171.2	167.1	111.2	139.66	177.9	171.5	111.8	110.7	179.8	171.8	166.40	167.3	112.0	
16	19.1	19.3	19.1	25.0	143.96	19.5	19.4	19.5	27.8	19.8	19.2	14.51	19.0	20.0	
17	15.9	15.5	15.7	15.6	175.48	30.5	24.0	30.4	24.5	102.5	106.4	21.73	110.3	19.4	
18	20.5	18.2	18.4	18.3	172.37	21.5	21.5	21.5	33.7	18.2	33.6	25.26	23.6	21.5	
19	32.1	18.7	18.9	18.1	27.00	33.3	33.4	33.1	21.8	20.8	21.7	33.64	33.7	33.2	
20	17.8	17.6	17.9	18.4	24.31	-	15.4	-	15.8	15.9	14.5	106.53	17.1	19.3	
1'		50.8													
2'															
3'	50.7											50.56	50.8		

a, b, and c may be interchanged for the same structure; (*) reassigned ^{13}C -NMR data in CDCl_3 ; (P) ^{13}C -NMR data in $\text{C}_5\text{D}_5\text{N}$; (D) ^{13}C -NMR data in DMSO-d_6 ; (A) ^{13}C -NMR data in acetone- d_6 ; (?) solvent not given

Table 5. ^{13}C -NMR data (in CDCl_3) of substituted diterpenes isolated from *Aristolochia* species.

Carbon	Compound / δ_{C} (in ppm)			Carbon	Compound / δ_{C} (in ppm)		
	24 [31]	25 [31]	26 [31]		24	25	26
1	40.3	40.4	40.4	1'	-	-	-
2	18.6	-	-	2'	112.7	112.8	112.5
3	41.9	42.0	42.0	3'	143.1	-	-
4	33.3	-	-	4'	147.5	146.8	146.2
5	56.0	56.1	56.2	4a'	-	-	-
6	20.5	-	20.5	4b'	131.0	-	131.0
7	42.1	42.0	42.0	5'	119.2	127.4	119.2
8	44.9	-	-	6'	131.0	130.5	-
9	56.7	56.6	56.5	7'	108.0	-	108.0
10	39.4	-	-	8'	156.9	130.2	156.9
11	18.3	-	-	8a'	120.2	128.5	120.2
12	26.3	27.1	27.4	9'	121.2	126.5	121.1
13	46.3	46.5	43.5	10'	145.9	-	-
14	37.2	37.5	38.1	10a'	-	118.3	119.2
15	53.3	53.4	51.0	11'	167.2	167.5	167.2
16	80.1	80.0	-	OCH ₂ O	102.4	103.0	102.4
17	69.6	70.2	63.7	OMe	56.2		56.2
18	33.6	33.6	33.6				
19	21.5	22.0	21.6				
20	17.8	18.0	17.8				

(--) Data not observed

The characteristic carbon chemical shifts for clerodane derivatives (except for **39** and **40**) are observed around δ_{C} 120.0-123.0 and 139.0-145.0, which are assigned to C-3 and C-4, respectively, as shown in Table 4 (see Figures 4 and 5). However, the carbon chemical shift ranges show higher values when C-2 is oxygenated, as is the case of **42** to **55** (Figure 5). The carbon chemical shifts around δ_{C} 38.0-40.0 (assigned to C-5 and C-9) and δ_{C} 36.0-38.0 (assigned to C-6 and C-8) are registered in the ^{13}C -NMR spectra of these compounds. Values close to δ_{C} 145.0 and 112.0 are assigned to the double bond between C-14 and C-15 in clerodane diterpenoids, as shown in **38-43**, **48**, and **54**. Besides, the values close to δ_{C} 160.0 and 115.0 were assigned to double bond between C-13 and C-14, respectively, and δ_{C} 73.0 for hydroxylated C-13 of these compounds.

Structure of furanoditerpenes (Figure 6) can be confirmed by carbon chemical shifts at δ_{C} 124.79, 108.40, 139.66, and 143.96 assigned to C-13, C-14, C-15, and C-16, respectively for **56**.

Despite the fact that **61** was not isolated from an *Aristolochia* species, its stereochemistry is close to that of **59** (see Figure 7). Thus, ^{13}C -NMR data of **61** were included in Table 4 to provide insights about the corresponding data of **59**. The carbon chemical shifts close to δ_{C} 145.0 and 112.0 are assigned to double bond between C-14 and C-15 in labdanes, as shown in Table 4 for **60**, **61**, and **67**. Values close to δ_{C} 160.0 and 115.0 can be assigned to double bond between C-13 and C-14 in **58** and **63-66**.

Table 5 shows the ^{13}C -NMR data of the substituted kaurane diterpenoids **24** to **26** (see Figure 3). These compounds present an aristolochic acid derivative bound to a kaurane diterpenoids at O-16 (for **24** and **25**) and O-17 (for **26**). Some carbon chemical shifts were not observed in the ^{13}C NMR data of **25** and **26**. As it would be expected only the carbon chemical shifts of C-13 to C-17 of **26** are different when comparing to **24** and **25**.

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Sample Availability: Samples of the compounds 27 and 45 are available from the authors.

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