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TWENTY-THREE FLAVONOIDS FROM *LONCHOCARPUS SUBGLAUCESCENS*

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Key Word Index—*Lonchocarpus subglaucescens*; Leguminosae; roots; chalcone; dihydrochalcone; dihydroflavanonol; flavan; flavanone; flavone; dibenzoylmethane; isoflavone; rotenoid.

Abstract—Chemical investigation of *Lonchocarpus subglaucescens* roots resulted in the isolation of 23 flavonoids, whose structures were elucidated by spectroscopic methods. Ponganone III, ovalichromene B, purpurenone, 12α-hydroxyrotenone, (2,3-*trans*-3,4-*trans*)-3,4,5,8-tetramethoxy-[2″,3″:7,6]-furanoflavan, 6″,6″-dimethylchromeno-[2″,3″:7,8]-flavone and 3′,4′-methylenedioxy-6″,6″-dimethylchromeno-[2″, 3″:7,8]-flavone had been previously isolated from other sources. The 16 new flavonoids are 6-methoxy-6″,6″-dimethylchromeno-[2″,3″:7,8]-flavanone, (2*S*)-5,6-dimethoxy-[2″,3″:7,8]-furanoflavanone, (2*R*,3*R*)-3,5,6-trimethoxy-[2″,3″,7,8]-furanoflavanonol, 3,4-methylenedioxy-2′-methoxy-6″,6″-dimethylchromeno-[2″,3″:4′,3′]-β-hydroxychalcone, (*Z*/*E*)-3,4-methylenedioxy-2′-methoxy-6″,6″-dimethylchromeno-[2″,3″:4′,3′]-9-methoxychalcone, (*E*)-2′-methoxy-6″,6″-dimethylchromeno-[2″,3″:4′,3′]-9-methoxychalcone, (2,4-*cis*)-3′,4′-methylenedioxy-4,5,8-trimethoxy-[2″, 3″:7,6]-furanoflavan, (2,4-*cis*)-4,5,6-trimethoxy-[2″,3″:7,8]furanoflavan, 3,4-dimethoxy-2′-hydroxy-6″,6″-dimethylchromeno-[2″,3″:4′,3′]-chalcone, 3,4-methylenedioxy-2′-hydroxy-3′,6′-dimethoxy-[2″,3″:4′,5′]-furanochalcone, (2,3-*trans*-3,4-*cis*-3,4,5,6-tetramethoxy-[2″,3″:7,8]-furanoflavan, (2,3-*trans*-3,4-*trans*)-3′,4′-methylenedioxy-3,4,5,8-tetramethoxy-[2″,3″:7,6]-furanoflavan, (2,3-*trans*-3,4-*cis*)-3′,4′-methylenedioxy-3,4,5,6-tetramethoxy-[2″,3″:7,8]-furanoflavan, 3,4-methylenedioxy-2′-methoxy-[2″,3″:4′,3′]-dihydrochalcone and 3′,4′-methylenedioxy-8-methoxy-5-hydroxy-6″,6″-dimethylchromeno-[2″,3″:7,6]-isoflavone.

INTRODUCTION

The genus *Lonchocarpus*, subfamily Papilonoideae, tribe Milletieae, consists of nearly 100 species distributed in tropical America, Africa and the Caribbean Islands. Some specialists include *Derris* and *Lonchocarpus* in the same genus. *Lonchocarpus* also shows a great vegetative and floral affinity with *Millettia*, *Pongamia* and *Piscidia*. Such morphological complexity has resulted in the adoption of controversial systems by different botanists. Taxonomic revision of *Lonchocarpus* in Brazil has recognized 23 species spread over two subgenera. *Lonchocarpus* subgenus *Lonchocarpus* was divided into five sections and comprises 15 species. *Lonchocarpus* subgenus *Punctati* (Benth) Tozzi was not divided into sections and contains eight species including *L. subglaucescens* Benth and *L. araripensis* Benth. The latter was previously classified as *Derris araripensis* Benth Ducke. *L. subglaucescens* occurs in southeast Brazil, while *L. araripensis* is found in the northeast. We now report the isolation of 23 flavonoids from the roots of *L. subglaucescens*.

RESULTS AND DISCUSSION

A petrol extract of *L. subglaucescens* roots was submitted to successive chromatographic analysis (column, chromatotron, TLC and preparative TLC), affording the flavonoids **1a–9**. Ponganone III (**4c**) [1], ovalichromene B (**4d**) [2, 3], purpurenone (**1a**) [4], 12α-hydroxyrotenone (**9**) [5–7], the 3,4-dimethoxyflavan (**6c**) [8] and the flavones (**7a** and **7b**) [9] were characterized by comparison of the respective spectral data with those published.

Compound **1a** now has its ^{13}C NMR spectrum registered for the first time and, together with DEPT, COSY and HETCOR spectra, allowed the assignment of all carbon shifts values (Table 1). Compound **1b** showed a ^{1}H NMR spectrum very similar to that of **1a** (Table 2). The absorptions at δ 16.58 (1H) and 7.05 ppm (1H) also are typical of a *Z*-dibenzoylmethane tautomer (**10**), preferentially assuming the conformation **11** where H-8 is under the anisotropic

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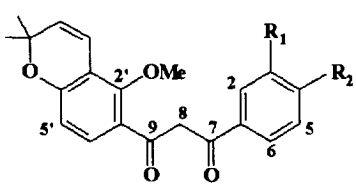
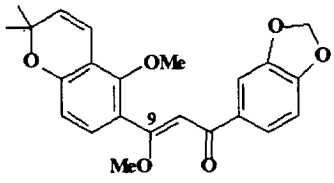


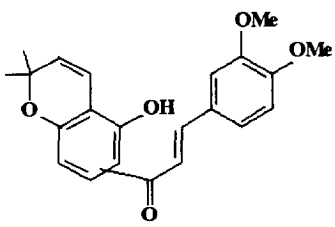
(1a) $R_1 = R_2 = H$

(1b) $R_1 + R_2 = OCH_2O$

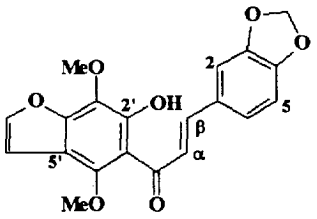


(Z)-(1c)

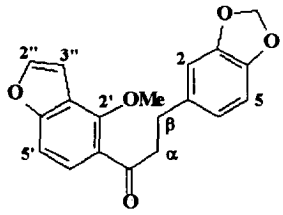
(E)-(1d)



(2a)



(2b)



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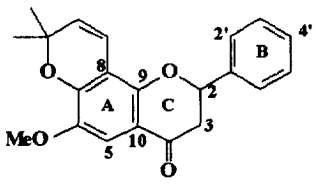
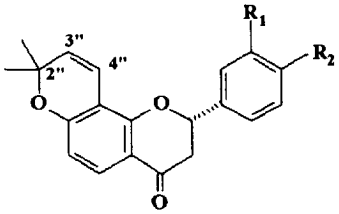
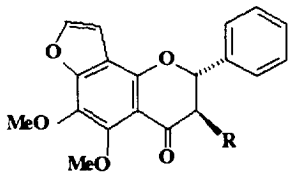


(4a)



(4c) $R_1 + R_2 = OCH_2O$

(4d) $R_1 = R_2 = OMe$



(4b) R= H

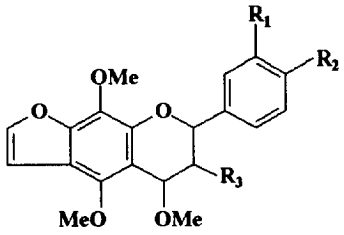
(5) R= OMe

effect of both rings and free from interaction with the methoxyl group located at C-2′ [10, 11]. The absorptions at δ 4.56 (*s*) and at 4.13 (*s*), both integrating less than 1H, correspond, respectively, to H-8 in conformer **10** and the methylene protons at C-8 in **1b**. These data indicate that conformer **11** predominates (Fig. 1). The chemical shifts of A-ring hydrogens are practically coincident in both compounds. The presence of a 3,4-methylenedioxy group was confirmed by the mass spectrum through the base peak at *m/z* 149, corresponding to C-7/C-8 bond cleavage. The ^{13}C NMR spectrum (Table 1) is also very similar to that of **1a**. The chemical shifts of A-ring carbons are practically superimposable and those of some B-ring carbons (C-2, C-5 and C-6) were confirmed by a HETCOR spectrum. In the UV spectrum band I (371 nm) suffered a bathochromic shift as compared with that of **1a** because of the methylenedioxy group on B ring.

Compounds **1c** and **1d** were isolated together as was evident in the ^1H NMR spectrum where all the absorptions occurred in pairs of different intensities. The spectral pattern is very similar to that of **1b** (Table 2). This time, however, instead of an absorption for the hydrogen of a strongly chelated hydroxyl group, the spectrum shows two singlets for methoxyl hydrogens, suggesting that **1c** and **1d** could be a mixture of the regioisomeric methylenol ethers derived from **1b** tautomers. By comparison of these data with those published for the methylenol ethers obtained from pongamol [12] we suggest that **1c** and **1d** are the configuration isomers (*Z*/*E*, 1:9) of the 9-methylenol ether derived from **1b**. The location of a methoxyl group at C-9 was further confirmed by the mass spectrum of the mixture, because the simultaneous loss of a methoxyl radical from C-2′ and cyclization, leading to an aromatic cation, is highly favoured and fits with the base peak at *m/z* 363 as shown in Scheme 1. NOE experiments made with the mixture of **1c** and **1d** also support the location of a methoxyl group at C-9 because by focusing on the absorptions corresponding to the main isomer (**1d**) we found that irradiation of the methoxyl at δ 3.89 caused an enhancement on the H-6′ signal. The ^{13}C NMR spectrum of the mixture only shows the peaks corresponding to the major compound **1d** (Table 1).

From the reaction of **1a** with diazomethane we obtained the 7- and 9-OMe regioisomers (2:1) both having the *Z* configuration (kinetic isomers) [12]. Each of them was passed through a silica gel column in order to be converted into the corresponding thermodynamic *E* isomer, but the respective NMR data showed that the 9-OMe regioisomer was obtained only in the *E* configuration (Fig. 2). After observing that **1c** is converted into **1d** on silica gel we believe **1d** is an artefact obtained during the isolation process of the natural product **1c**.

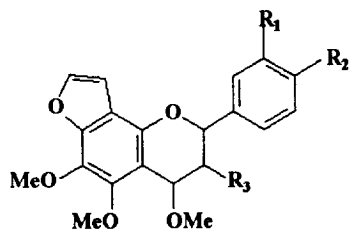
Compound **2a** has a ^1H NMR spectrum compatible



(6c) R_1= R_2= H; R_3= OMe

(6e) R_1 + R_2= OCH_2O; R_3= OMe

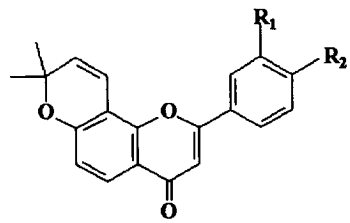
(6a) R_1 + R_2= OCH_2O; R_3= H



(6d) R_1= R_2= H; R_3= OMe

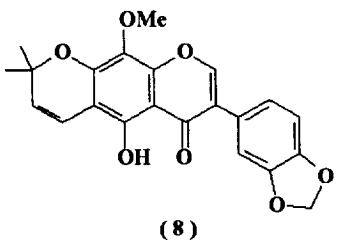
(6f) R_1 + R_2= OCH_2O; R_3= OMe

(6b) R_1= R_2= R_3= H



(7a) R_1= R_2= H

(7b) R_1 + R_2= OCH_2O



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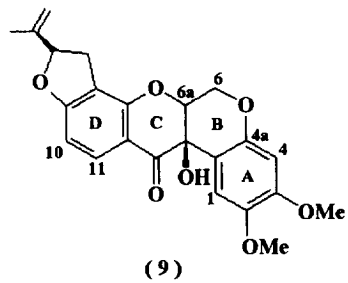

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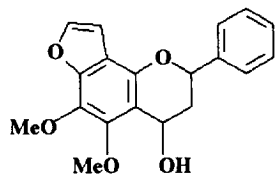


2,4-cis (16)

2,4-trans (17)

with a chalcone skeleton once that it shows the characteristic pair of doublets corresponding to the *trans*-α,β-hydrogens [13]. The signal of a hydrogen bonded hydroxyl group, a 2,2-dimethylchromene ring and two vicinal aromatic hydrogens lead us to the A-ring structure. Singlets of two methoxyl groups together with those of three aromatic hydrogens *ortho* and *meta* coupled are compatible with a 3′,4′-dimethoxy substituted B ring. The chalcone skeleton was confirmed by the ^{13}C NMR spectrum where carbonyl, C-α and C-β absorbed as expected [14, 15]. The carbon absorptions corresponding to A and B rings are also compatible (Table 1). The mass spectrum shows the molecular ion peak [M = 366 (75%)]$^+$ and the base peak is at m/z 351 [M − 15]$^+$. Other peaks correspond to RDA fragmentation coming from a previous intramolecular equilibrium (chalcone flavanone), which is typical of a 2-OH-chalcone (Scheme 2).

Compound **2b** is also a chalcone, once that its ^1H NMR spectrum shows a pair of doublets corresponding to *trans*-α,β-hydrogens. This time there is a singlet corresponding to a methylenedioxy group together with an ABX absorption pattern in the aromatic region, suggesting a 3′,4′-methylenedioxy B ring. Other signals corresponding to furan hydrogens, a hydrogen bonded hydroxyl group and two methoxyl groups lead us to an A-ring structure. Through a NOE experiment the furan was found to be linearly fused with the A ring because H-3″ irradiation caused an enhancement on one methoxyl signal.

Compound **3** shows in the ^1H NMR spectrum triplets expected for H-α and H-β hydrogens in a dihydrochalcone skeleton. Signals of furan hydrogens, a methoxyl and *ortho* coupled hydrogens lead us to an A-ring structure while those of a methylenedioxy together with an ABX absorption pattern brought us to a B ring. The splitting of H-3″ signal corresponds to the long range coupling ($^nJ_{CH}$) with H-5′. In the ^{13}C NMR spectrum the peaks for Cα and Cβ were inverted in DEPT. All carbons absorptions are shown in Table 1. The mass spectrum confirms structure **3** since the base peak (m/z 175) corresponds to a carbonyl Cα-bond cleavage.

Compound **4a** was isolated together with two minor flavonoids in a ratio of 3:1:1 as determined by the ^1H NMR spectrum of the mixture. The molecular structure could be assigned through the analysis of the most prominent signals. The presence of a flavanone was evident by the observed double doublets with the

Table 1. ^{13}C NMR spectra of compounds **1a**, **1b**, **1d**, **2a** and **3**

C	1a	1b	1d	2a	3
1	135.7	130.4	131.0	127.8	135.5
2	127.0	107.2	107.7	110.2	108.9
3	128.6	148.2	148.0*	151.6*	145.7†
4	132.1	151.2	151.0*	149.3*	147.5†
5	128.6	108.2	108.5	111.2	106.5
6	127.0	122.8	124.1	123.3	121.1
7 (β)	185.2	185.1	169.0	144.4	30.4
8 (α)	96.7	96.0	99.8	118.0	45.5
9 (C=O)	184.4	183.1	134.6	191.9	201.2
1′	121.8	121.5	121.8	109.5	124.8*
2′	156.2	156.0	154.2	160.9	153.9
3′	115.1	115.2	116.8	114.1	118.3*
4′	157.6	157.4	155.4	159.7	159.0
5′	113.0	113.0	112.2	108.2	108.2
6′	130.7	139.7	130.1	130.5	126.7
2″	77.3	76.9	76.3	77.8	144.7
3″	130.7	130.6	130.4	128.1	105.7
4″	116.4	116.5	117.2	115.9	—
2‴	—	101.8	101.7	—	100.7
OMe (C-2′)	62.6	62.5	62.1	—	60.6
Me (C-2″)	28.2	28.2	28.1	28.4	—
OMe (C-9)	—	—	56.3	—	—
OMe (C-3′)	—	—	—	56.0	—
OMe (C-4′)	—	—	—	56.0	—

*,†Interchangeable values.

typical chemical shifts and coupling constants expected for C-ring hydrogen absorptions. A methoxyl group and a 2,2-dimethylchromene moiety must be on the A ring because of a sharp singlet for a single aromatic hydrogen and the multiplet (5H) typical for a free B ring. The ^{13}C NMR spectrum (Table 3) is also compatible with a flavanone having the substituents located on the A ring. The corresponding DEPT 90° and 135° showed the presence of $8C_0$, 9CH, $1CH_2$ and 3Me. Based on these data we can suggest four structural possibilities (**13**–**15** and **4a**) concerned with alternative substitution patterns of the A ring (Fig. 3). Obovatin methyl ether (**13**) was previously isolated from *L. costaricensis* [16] and *Tephrosia obovata* [17], but its NMR data are not coincident. Structure **14** can be ruled out because the chemical shifts expected for C-8 and H-8 would be much higher than those observed for the only CH left on the A ring. Finally, we choose **4a** because in the difference NOE spectrum, irradiation of the methoxyl group at 3.88 ppm caused an enhancement of the singlet at 7.28 ppm and irradiation of H-4″ affected only the H-3″ signal.

The two minor flavonoids present in the mixture were identified with the flavan (**6c**), which will be described later, and (*E*)-9-OMe-purpurenone (**1e**), which we have already described as one of the products obtained from the reaction of **1a** with diazomethane. In fact GC–mass spectrometric analysis of the mixture separated three compounds. The mass spectrum of the main one was interpreted according to the expected C-ring RDA cleavage. In the NOE difference spectrum of the mixture, irradiation of the singlet at 6.27 ppm caused enhancement of a methoxyl group signal at 3.9 ppm and of the aromatic protons *ca* 7.8 ppm. These findings are in agreement with the spatial proximity of H-8, 9-OMe, H-2 and H-6 on structure **1e** and allow the assignment of the 9-OMe chemical shift, precisely.

Compound **5** showed in the ^1H NMR spectrum the typical doublets expected for C-ring hydrogen absorptions of a flavanonol while the singlet of an aliphatic methoxyl group suggests the corresponding methyl ether. The presence of two aromatic methoxyl singlets, the hydrogens doublets of a furan and a multiplet corresponding to five aromatic hydrogens indicate a totally substituted A ring and a free B ring. In the NOE difference spectrum, irradiation of H-3″ caused enhancement only of H-2″ signal, leading us to the conclusion that the furan is angularly fused with an A ring. The ^{13}C NMR spectrum (Table 3) is totally compatible, and the presence of 8 C_0, 9 CH and 3 Me was confirmed by DEPT 90° and 135°. The mass spectrum showed the molecular ion [M + 354] (5%). The fragments at *m/z* 220 (100%) and *m/z* 134 (17%) coming from C-ring RDA correspond to A- and B-ring moieties, respectively. The positive Cotton effect observed in the ORD curve is in agreement with 2*R*,3*R* absolute configuration [18].

Table 2. ^1H NMR spectra of compounds **1a**–**1d**

H	1a	1b	1c	1d
2	7.96 (*dd*, 8.2, 1.5 Hz)	7.46 (*d*, 1.6 Hz)	7.33 (*d*, 1.7 Hz)	7.61 (*d*, 1.6 Hz)
6		7.58 (*dd*, 8.2, 1.6 Hz)	7.45 (*dd*, 8.1, 1.7 Hz)	7.53 (*dd*, 8.2, 1.6 Hz)
3, 4	7.45–7.56 (3H, *m*)	—	—	—
5		6.89 (*d*, 8.2 Hz)	6.77 (*d*, 8.1 Hz)	6.82 (*d*, 8.2 Hz)
8	7.16 (*s*)	7.05 (*s*)	6.20 (*s*)	6.20 (*s*)
5′	6.67 (*d*, 8.5 Hz)	6.68 (*d*, 8.5 Hz)	6.52 (*d*, 8.3 Hz)	6.61 (*d*, 8.3 Hz)
6′	7.75 (*d*, 8.5 Hz)	7.73 (*d*, 8.5 Hz)	6.96 (*d*, 8.3 Hz)	7.15 (*d*, 8.3 Hz)
3″	5.70 (*d*, 9.9 Hz)	5.70 (*d*, 10.0 Hz)	5.59 (*d*, 9.8 Hz)	5.71 (*d*, 10.0 Hz)
4″	6.66 (*d*, 9.9 Hz)	6.66 (*d*, 10.0 Hz)	6.55 (*d*, 9.8 Hz)	6.63 (*d*, 10.0 Hz)
2‴	—	6.06 (*s*)	5.99 (*s*)	6.02 (*s*)
OMe	3.80 (*s*)	3.80 (*s*)	3.71 (*s*)	3.76 (*s*)
Me_2	1.46 (*s*)	1.46 (*s*)	1.41 (*s*)	1.61 (*s*)
OH	16.90 (*s*)	16.98 (*s*)	—	—
OMe (C-9)	—	—	3.89 (*s*)	3.80 (*s*)

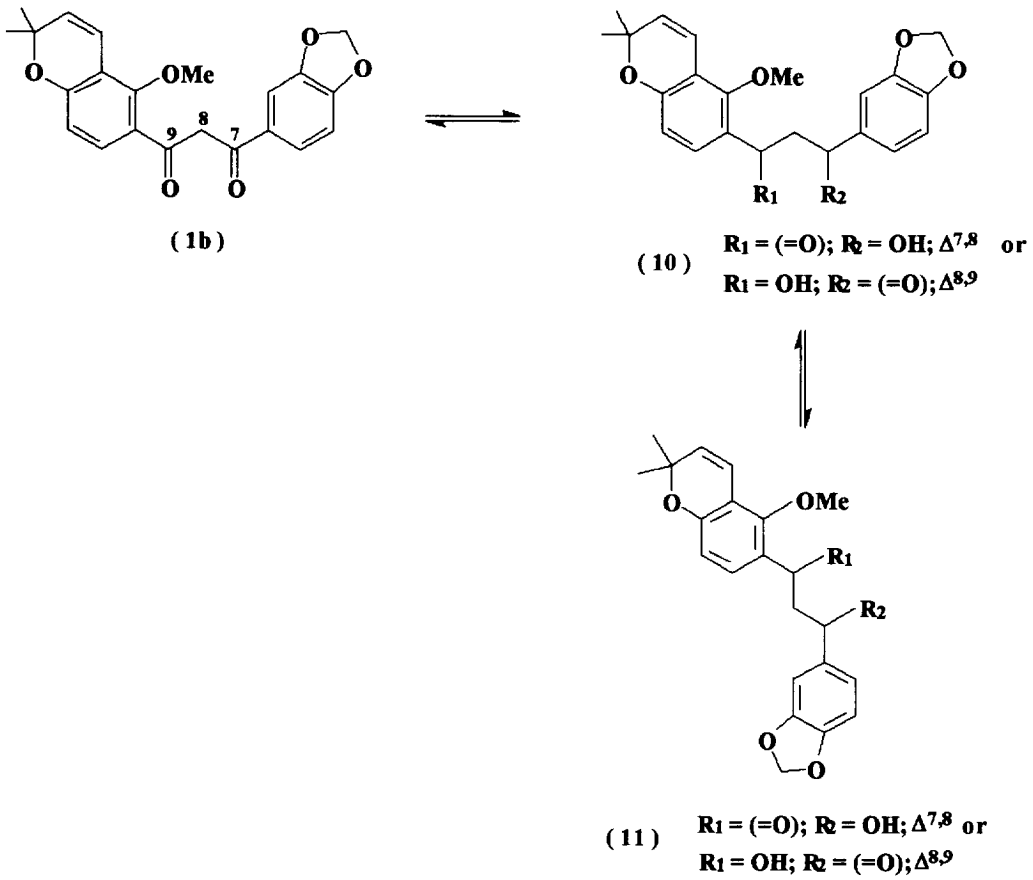
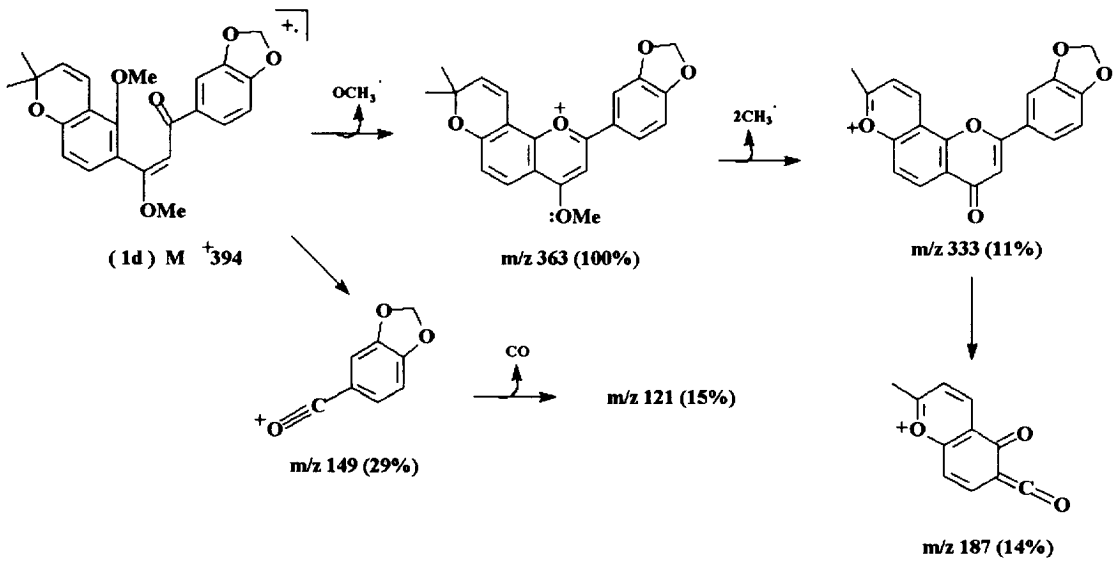


Fig. 1. Keto–enol and conformational equilibrium of compound **1b**.

Compound **6a** showed in the ^{1}H NMR spectrum (Table 4) a double doublet, a triplet and two multiplets of eight lines each (*ddd*) as expected for C-ring hydrogens (H-2, H-4 and H-3) in a 4-substituted flavan. A sharp singlet of an aliphatic methoxyl group suggest a 4-methoxyl flavan derivative. Doublets for the hydrogens of a furan, two singlets for aromatic methoxyl groups and a sharp singlet for a methylenedioxy group, together with the signals for three left aromatic hydrogens suggest two structural alternatives (Fig. 4). The



Scheme 1. Fragmentation pathway of compound **1d**.

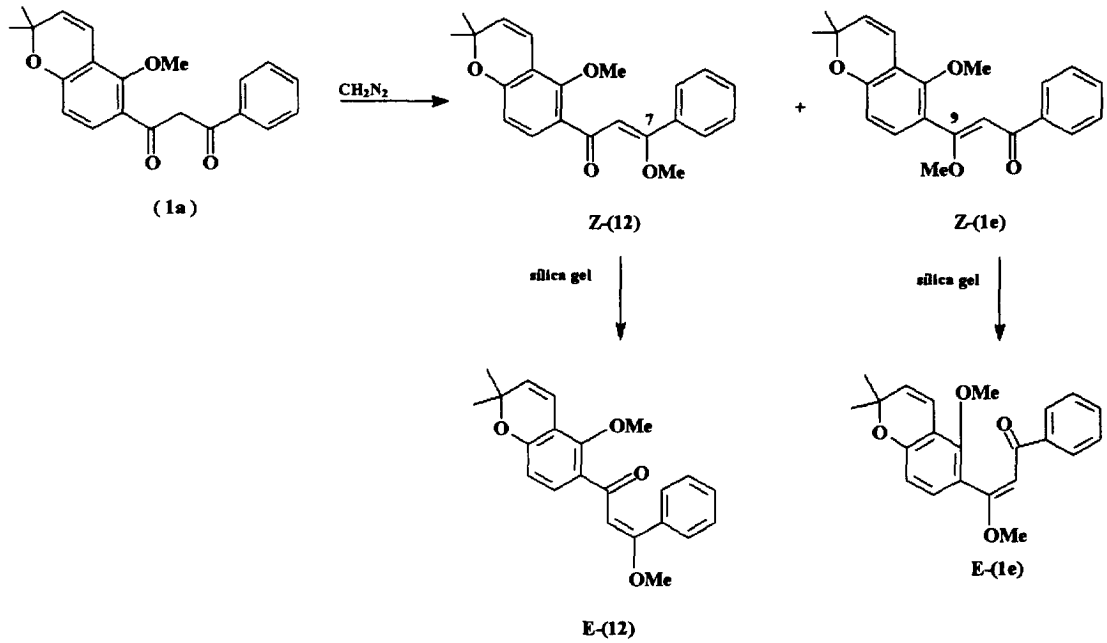
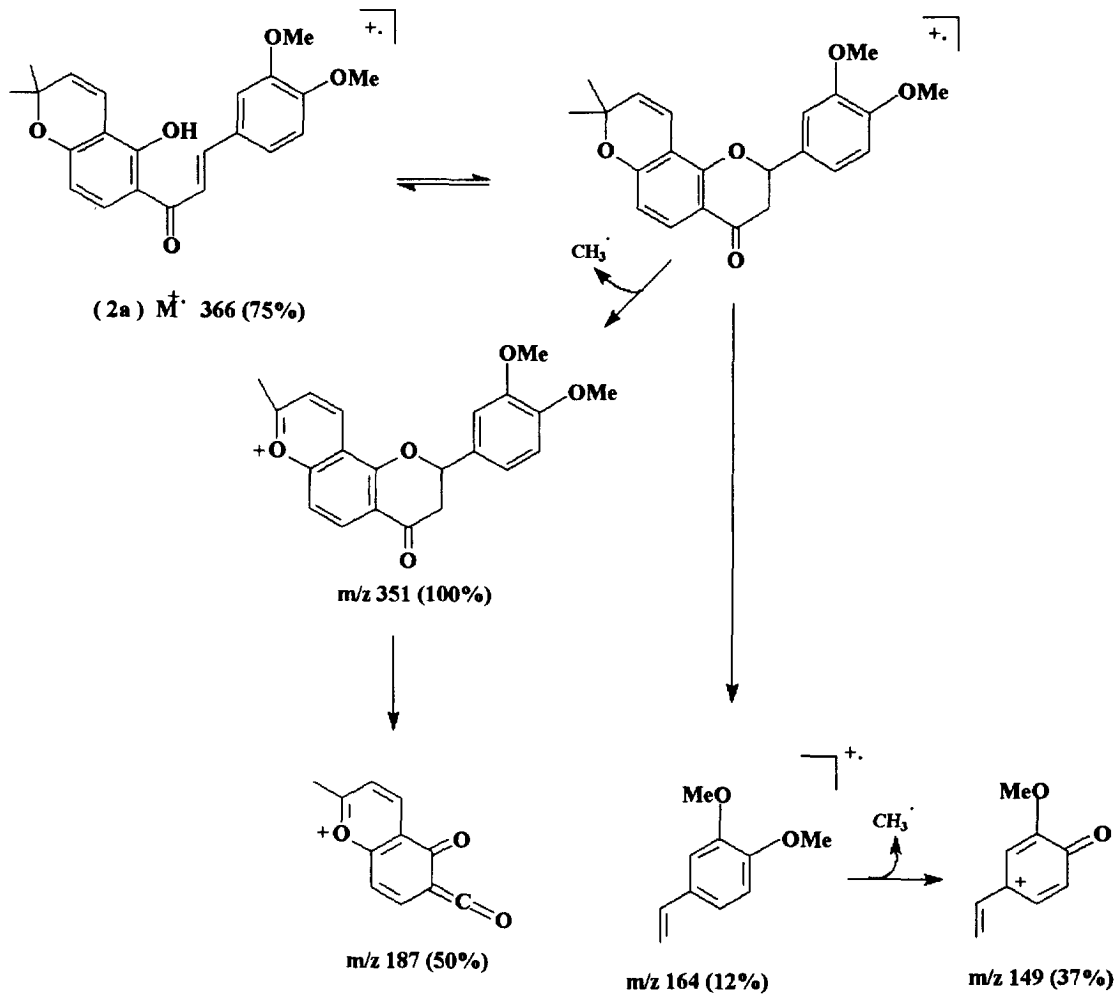


Fig. 2. Reaction of compound **1a** with diazomethane and products isomerization on silica gel column.



Scheme 2. Fragmentation pathway of compound **2a**.

Table 3. ^{13}C NMR spectra of compounds **6a**–**6f**, **4a** and **5**

C	6a	6b	6c	6d	6e	6f	4a	5
2	77.3	77.3	80.5	70.4	81.1	79.7	79.9	82.5*
3	35.8	35.7	82.9	82.0	83.7	82.6	44.4	82.4*
4	70.4	70.8	74.5	74.7	75.2	75.4	190.7	190.0
5	147.8*	149.3*	147.6	148.6	147.9	148.6	99.8	150.9†
6	113.9	133.9	114.1	133.4	114.2	132.3	152.7	134.7
7	148.4*	148.7*	148.9	148.3	148.8	148.3	169.2	151.9†
8	128.0	114.9	130.0	114.2	130.0	114.3	110.5	114.7
9	146.2	144.9	145.4	143.0	145.4	143.1	149.5	149.2†
10	112.2	112.4	111.4	110.6	111.5	110.9	112.0	109.9
1′	135.0	141.6	139.1	138.4	133.0	133.5	139.1	136.5
2′	106.7	128.9	126.6	126.5	107.5	107.2	126.0	128.6
3′	147.3†	126.3	128.2	128.2	147.6‡	147.6‡	128.7	127.1
4′	146.9†	128.2	127.7	127.7	147.5‡	147.2‡	129.0	128.9
5′	108.1	126.3	128.2	128.2	108.2	108.4	128.7	127.1
6′	119.4	128.9	126.6	126.5	120.7	120.3	126.0	128.6
2″	143.4	144.2	143.5	143.7	143.9	143.8	78.0	144.9
3″	104.7	104.7	104.8	104.4	105.0	104.4	128.6	105.1
4″	—	—	—	—	—	—	116.1	—
OMe (C-3)	—	—	58.3	58.61*	58.6*	58.8*	—	60.2
OMe (C-4)	55.8	56.0	56.7	57.01*	57.0*	57.2*	—	—
OMe (C-5)	60.8‡	61.2†	60.6	60.98†	60.8†	61.0†	—	61.5‡
OMe (C-6 or C-8)	61.3‡	61.8†	61.3	61.56†	61.5†	61.5†	56.3	62.3‡
2‴	101.0	—	—	—	101.2	101.1	—	—
Me (C-2″)	—	—	—	—	—	—	28.3	—

*,†,‡Interchangeable values.

relative configuration of 4-substituted flavans has been assigned by the appearance of a H-4 signal and the summation of the respective coupling constant values. It occurs as a double doublet in the *cis* isomer ($J_{3a,4} + J_{3b,4}$ = 16.4–17.7 Hz) and as a triplet in the *trans* isomer ($J_{3a,4} + J_{3b,4}$ = 5.0–6.0 Hz) [19–22]. In the case of **6a** the H-4 signal is a triplet, but $J_{3a,4} + J_{3b,4}$ = 14.40 Hz is nearer those usually obtained for the *cis* isomers. In the NOE difference spectrum (see the arrows in Fig. 4) several irradiations were made and the results provided the following conclusions:

(a) The furan is linearly fused with the A ring on

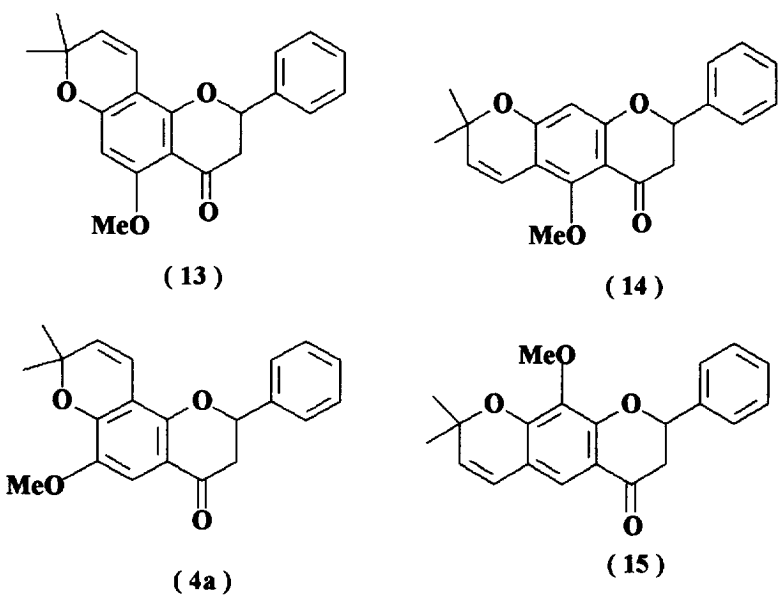


Fig. 3. Structural alternatives for compound **4a**.

Table 4. ^{1}H NMR spectra of compounds **6a**, **6b**, **6e** and **6f**

H	6b	6a	6e	6f
2	5.17 (*dd*, 9.7, 3.0 Hz)	5.00 (*dd*, 9.9, 3.3 Hz)	4.84 (*d*, 6.9 Hz)	4.98 (*d*, 7.2 Hz)
3ax	2.62 (*ddd*, 13.9, 9.7, 7.1 Hz)	2.34 (*ddd*, 13.9, 9.9, 7.2 Hz)	—	—
3eq	2.40 (*ddd*, 13.9, 7.1, 3.0 Hz)	2.57 (*ddd*, 13.9, 7.2, 3.3 Hz)	—	—
3	—	—	3.84 (*dd*, 6.9, 4.3 Hz)	3.83 (*dd*, 7.2, 4.8 Hz)
4	4.84 (*t*, 7.1 Hz)	4.92 (*t*, 7.2 Hz)	4.79 (*d*, 4.3 Hz)	4.66 (*d*, 4.8 Hz)
2′		6.98 (*d*, 1.6 Hz)	7.01 (*d*, 1.6 Hz)	6.96 (*d*, 1.6 Hz)
3′,4′		—	—	—
5′	7.40 (5H, *m*)	6.79 (*d*, 8.1 Hz)	6.81 (*d*, 8.1 Hz)	6.80 (*d*, 8.0 Hz)
6′		6.89 (*dd*, 8.1, 1.6 Hz)	6.93 (*dd*, 8.1, 1.6 Hz)	6.90 (*dd*, 8.0, 1.6 Hz)
2″	7.51 (*d*, 2.1 Hz)	7.49 (*d*, 2.4 Hz)	7.51 (*d*, 1.9 Hz)	7.50 (*d*, 2.1 Hz)
3″	6.82 (*d*, 2.1 Hz)	6.84 (*d*, 2.4 Hz)	6.87 (*d*, 1.8 Hz)	6.80 (*d*, 2.1 Hz)
OMe (C-3)	—	—	3.29 (*s*)*	3.30 (*s*)*
OMe (C-4)	3.37 (*s*)	3.38 (*s*)	3.40 (*s*)*	3.44 (*s*)*
OMe (C-5)	3.99 (*s*)*	4.02 (*s*)*	4.06 (*s*)†	3.99 (*s*)†
OMe (C-6 or C-8)	4.07 (*s*)*	4.05 (*s*)*	4.02 (*s*)†	4.07 (*s*)†
2‴	—	5.96 (*s*)	5.97 (*s*)	5.97 (*s*)

*,†Interchangeable values.

account of the enhancements observed after H-3″ and aromatic methoxyl irradiations.

(b) The H-2 chemical shift was precisely determined because its irradiation caused a great enhancement of H-2′ and H-6′ signals.

(c) H-2 and H-4 chemical shifts are very close so that it is impossible to observe a NOE effect between them. However, the relative configuration of the C ring must be *cis* because irradiation of H-2 and H-4 both caused enhancement of the same hydrogen attached on C-3.

The ^{13}C NMR (Table 3) is also compatible. The presence of $9C_0$, 7CH, $7CH_2$ and 3Me was confirmed by DEPT 90° and 135°. The mass spectrum shows the molecular ion [M + 384] (54%) and the peaks corresponding to the fragmentation pathway in Scheme 3.

Compound **6b** is very similar to **6a** as can be shown by the respective ^{1}H NMR data (Table 4). This time, a multiplet corresponding to five aromatic hydrogens suggests a free B ring. The ^{13}C NMR data (Table 3) were confirmed by DEPT 90° and 135°, which gave $7C_0$, 9CH, $1CH_2$ and 3Me. The results of the NOE difference spectrum suggest the same relative configuration (2,4-*cis*) and also allowed the assignment of H-2 and H-4 signals unambiguously. The furan, however, must be angularly fused once that H-3″ irradiation caused enhancement only on the H-2″ signal. After standing in chloroform for a weekend, **6b** was transformed into two new diastereoisomeric alcohols: 2,4-*cis* (**16**) and 2,4-*trans* (**17**), which were separated by preparative TLC. The ^{1}H NMR data showed that in **16** the H-2 signal is downfield because of the *cis*-hydroxyl on C-4, and the H-4 signal appears as a double doublet. In the case of **17** the H-2 signal is upfield and the H-4 signal is a triplet. The ^{13}C NMR data are also compatible and were confirmed by DEPT 90° and 135°.

Compounds **6c** and **6d** showed much simpler signals corresponding to C-ring hydrogens in the ^{1}H NMR spectrum, because instead of two eight-line multiplets for C-3 hydrogens, there is a downfield double doublet for one hydrogen, while the H-2 and H-4 signals are doublets. Both spectra also show signals for a furan, a free B ring and four methoxyl groups, leading us to suggest that **6c** and **6d** might be two diastereoisomeric 3,4-dimethoxy flavans. The enhancements observed in the NOE difference spectrum of **6c** allowed the following conclusions: (a) the furan is linear to the A ring and not angular as it had been suggested before [8]; (b)

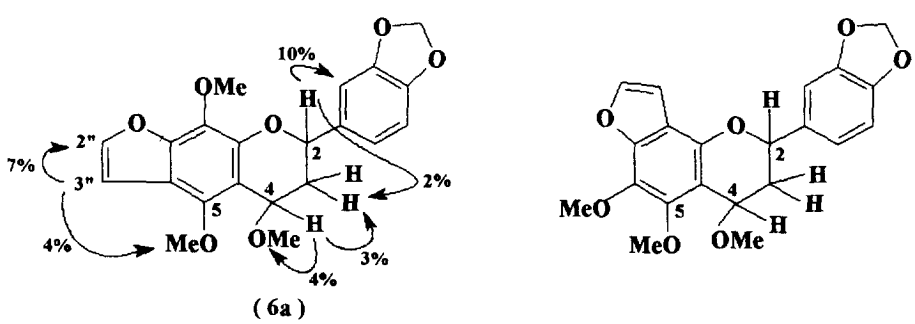
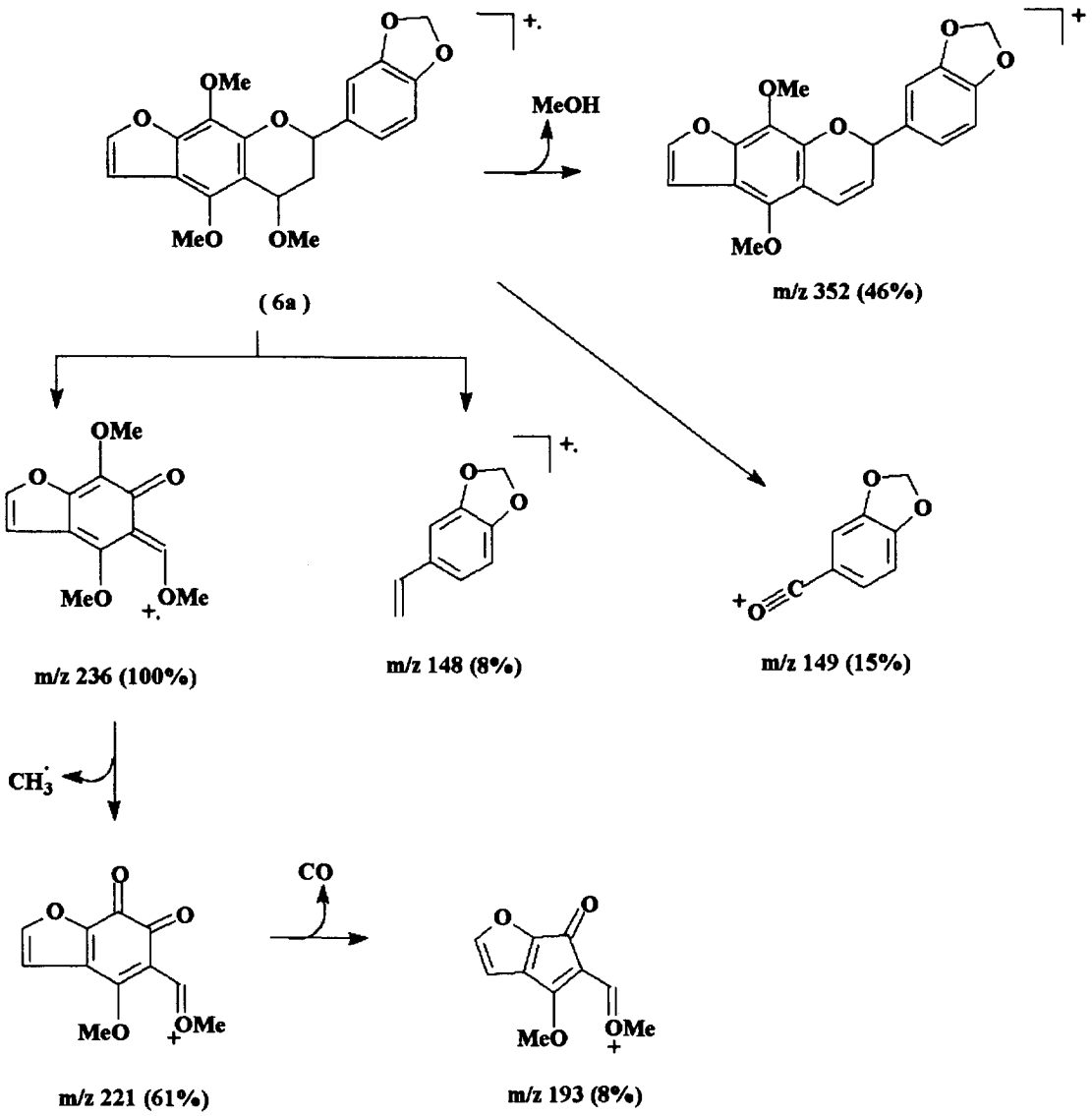


Fig. 4. Structural alternatives for compound **6a** and observed NOE effects.



Scheme 3. Fragmentation pathway of compound **6a**.

unambiguous determination of H-2 and H-4 chemical shifts; and (c) relative configuration of the C ring remains unclear.

In the case of **6d** the NOE experiment showed that the furan is angular to the A ring and also allowed the assignment of H-2 and H-4 chemical shifts, but again the relative configuration of C ring could not be determined.

However, going back to the ^{1}H NMR data we see that in **6c**, H-2 is shielded and H-4 is deshielded while the opposite is found in **6d**. The coupling constant value for J_{H2-H3} is the same in both compounds and fits with *trans* orientation, while those for J_{H4-H3} are very close and could be taken as being due to 3,4-*cis* or 3,4-*trans* orientations. Considering that a half-chair conformation is preferentially assumed by the C ring, we can suggest the alternatives shown in Fig. 5. Molecular models indicate almost identical dihedral angles in both diastereoisomers (A and B), which could be used to explain the observed coupling constant values. The H-2 chemical shift, however, should reflect the influence of the methoxyl groups on C-4 being upfield or downfield, respectively, corresponding to 2,3-*trans*-3,4-*trans* or 2,3-*trans*-3,4-*cis*. Based on these findings we now suggest that **6c** is 2,3-*trans*-3,4-*trans* and **6d** is 2,3-*trans*-3,4-*cis*, respectively, having the furan linear and angular to the A ring. The ^{13}C NMR spectra (Table 3) are also compatible and were confirmed by DEPT 90° and 135°. In the case of **6c**, COLOC and HETCOR spectra, respectively, gave A-ring and C-ring carbon chemical shifts. Those of C-1, C-10 and C-1′ were defined by exclusion and comparison with other 3,4-dimethoxyflavans found in the literature [14, 15].

According to NMR data (Tables 3 and 4) compounds **6e** and **6f** are closely related to **6c** and **6d**, but instead

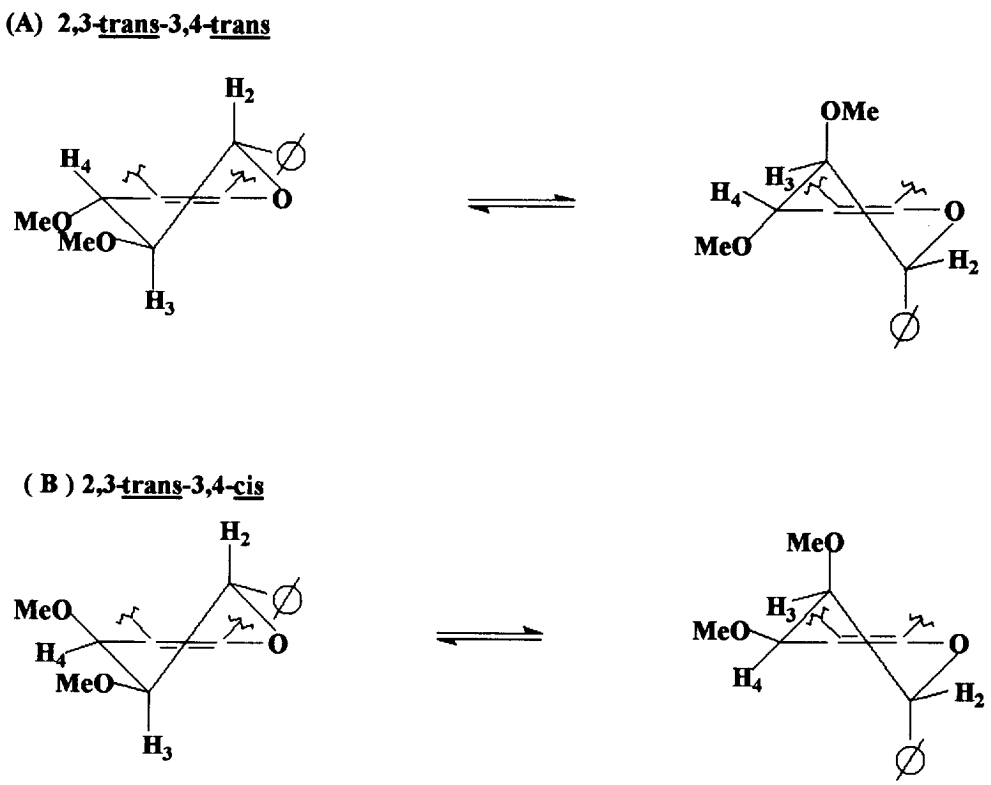


Fig. 5. Possible relative configuration for compounds **6c** and **6d**.

of a free B ring both have a 3,4-methylenedioxy group. NOE difference spectra were also taken in order to find out the furan orientation as well as H-2 and H-4 chemical shifts. The relative configuration of the C ring was determined as described above for **6c** and **6d**. The main peaks observed in the mass spectra of compounds **6c–6f** correspond to C-ring RDA cleavage and loss of methyl or methoxyl radicals, similar to the fragmentation pathway in Scheme 3.

Compound **6c** was previously isolated from *D. araripensis* (*L. araripensis*). It was suggested that the furan should be angular, based on spectral data (^{1}H NMR and mass spectral) and biogenesis. Nothing was mentioned of the relative configuration [8]. Compounds **4b** and **5** showed ORD curves according to 2*S* and 2*R*,3*R* configurations, respectively, leading us to the conclusion that compound **6b** is 2*S*,4*S* and **6d** is 2*R*,3*S*,4*S* once that the relative configuration could be determined as described above, and all of them belong to the same biosynthetic pathway.

Compound **8** was characterized through its ^{1}H NMR spectrum, where the sharp singlet at 7.73 ppm (1H) is typical of an isoflavone H-2 signal. There are also absorptions for a hydrogen bonded hydroxyl, two methoxyl groups, a 2,2-dimethylchromene moiety, a methylenedioxy group and three aromatic hydrogens. Linear fusion of the A ring with 2,2-dimethylchromene was chosen after comparison with data published for the angular analogue previously isolated [23].

EXPERIMENTAL

UV: $CHCl_3$. IR: KBr or film. ^{1}H NMR: in $CDCl_3$, at 300 MHz with TMS as int. standard. ^{13}C NMR: in $CDCl_3$, at 75.5 MHz with TMS as int. standard. EIMS: 70 eV. Mps are uncorr.

Plant material. Roots of *L. subglaucescens* were collected at Fazenda Sta Eliza, Campinas (SP), Brazil, in 1990. A voucher sample is deposited in the Herbarium of Campinas State University (UNICAMP).

Extraction and separation. Roots (1 kg) were powdered and extracted with hot petrol, then $CHCl_3$ and finally MeOH. Concn of the petrol extract gave a brown oil (7.2 g), part of which (7.0 g) was subjected to CC over silica gel. Elution with petrol followed by successive prep. TLC gave **1b** (14.1 mg). Elution with petrol containing 5% EtOAc followed by chromatotron and prep. TLC gave **6b** (15.7 mg). Elution with 7.5% EtOAc gave a mixt. which was sepd by prep. TLC to give more **3** (22.1 mg), **6d** (5 mg) and **4c** (5.7 mg). Elution with 25% EtOAc gave a mixt. of 6 compounds, which were sepd by chromatotron, furnishing **1a** (238.4 mg) and **7a** (9.8 mg), then prep. TLC gave **2a** (2.5 mg), **6e** (2.9 mg), **6c** (34.3 mg) and a mixt. **4a** + **1e** + **6c** (4.7 mg). Elution with 50% EtOAc gave a mixt. of 5 compounds which were sepd by several prep. TLC, furnishing **4b** (2.34 mg), **5** (3.18 mg), **6a** (7.66 mg), **2b** (1.24 mg) and again **7a** (34.5 mg). Elution with EtOAc containing 50% MeOH gave a pptd **7b** (37.7 mg) and prep. TLC of the supernatant gave **1b**

(69.2 mg), **4d** (10.9 mg), **6f** (5.1 mg) and a mixt. of **1c** and **1d** (8.3 mg). Elution with MeOH gave a mixt. which was sepd by chromatotron to give more **8** (6.7 mg) and followed by prep. TLC to give **9** (23.7 mg).

2′-Methoxy-6″,6″-dimethylchromeno-[2″,3″:4′,3′]-β-hydroxychalcone (**1a**). Mp: 75.9°. UV λ_{max} nm (log ε): 242 (4.28), 362 (4.48). IR ν_{max} cm^{-1} (film): 2976, 1580, 1458, 1114, 1076. ^{1}H NMR: see Table 2; ^{13}C NMR: see Table 1. EIMS *m/z* (rel. int.): 336 (13), 321 (53), 305 (53), 217 (20), 202 (27), 187 (20), 175 (27), 160 (20), 145 (13), 105 (87), 77 (100).

3,4-Methylenedioxy-2′-methoxy-6″,6″-dimethylchromeno-[2″,3″:4′,3′]-β-hydroxychalcone (**1b**). Oil. UV λ_{max} nm (log ε): 241 (4.18), 371 (4.35). IR ν_{max} cm^{-1} (film): 2928, 1590, 1458, 1254, 1112, 1072 e 1038. ^{1}H NMR: see Table 2; ^{13}C NMR: see Table 1. EIMS *m/z* (rel. int.): 380 (9), 365 (29), 349 (29), 217 (6), 202 (9), 187 (17), 175 (91), 160 (18), 149 (100).

(Z/E)-3,4-Methylenedioxy-2′-methoxy-6″,6″-dimethylchromeno-[2″,3″:4′,3′]-9-methoxychalcone (**1c** *and* **1d**). UV λ_{max} nm (log ε): 242 (4.49), 289 (4.30), 319 (4.31). IR ν_{max} cm^{-1} (KBr): 2974, 1655, 1606, 1478, 1238, 1038 e 787. ^{1}H NMR: see Table 2; ^{13}C NMR: see Table 1. EIMS *m/z* (rel. int.): 363 (100), 187 (14), 149 (29), 121 (15), 65 (23).

3,4-Dimethoxy-2′-hydroxy-6″,6″-dimethylchromeno-[2″,3″:4′,3′]-chalcone (**2a**). UV λ_{max} nm: 380, 268, 240. IR ν_{max} cm^{-1} (film): 2900, 1620, 1550, 1500, 1250, 1110. ^{1}H NMR: 7.42 (1H, *d*, *J* = 15.3 Hz, H-α), 7.84 (1H, *d*, *J* = 15.3 Hz, H-β), 7.16 (1H, *d*, *J* = 1.8 Hz, H-2), 6.91 (1H, *d*, *J* = 8.1 Hz, H-5), 7.25 (1H, *dd*, *J* = 8.1, 1.8 Hz, H-6), 6.39 (1H, *d*, *J* = 8.8 Hz, H-5′), 7.7 (1H, *d*, *J* = 8.8 Hz, H-6′), 5.60 (1H, *d*, *J* = 10.0 Hz, H-3″), 6.76 (1H, *d*, *J* = 10.0 Hz, H-4″), 1.47 (6H, *s*, 2″-Me_2), 13.78 (1H, *s*, 2′OH), 3.97, 3.94 (2 × 3H, 2 × *s*, 3-OMe, 4-OMe). ^{13}C NMR: see Table 1. EIMS *m/z* (rel. int.): 366 (75), 351 (100), 187 (50), 164 (12%), 149 (37).

3,4-Methylenedioxy-2′-hydroxy-3′,6′-dimethoxy-[2″,3″:4′,5′]-furanochalcone (**2b**). ^{1}H NMR: 7.46 (1H, *d*, *J* = 16.0 Hz, H-α), 7.67 (1H, *d*, *J* = 16.0 Hz, H-β), 7.17 (1H, *s* large, H-2), 6.84 (1H, *d*, *J* = 8.0 Hz, H-5), 6.11 (1H, *dd*, *J* = 8.0, 1.6 Hz, H-6), 7.66 (1H, *d*, *J* = 2.2 Hz, H-2″), 6.97 (1H, *d*, *d*, *J* = 2.2 Hz, H-3″), 6.03 (2H, *s*, H-2‴), 12.10 (1H, *s*, 2′-OH), 3.98, 4.02 (2 × 3H, 2 × *s*, 5′-OMe, 6′-OMe).

3,4-Methylenedioxy-2′-methoxy-[2″,3″:4′,3′]-dihydrochalcone (**3**). Mp 79°. UV λ_{max} nm (log ε): 242 (4.44). IR ν_{max} cm^{-1} (KBr): 2936, 1665, 1500, 1362, 1250, 1039, 703. ^{1}H NMR: 2.96 (1H, *t*, *J* = 7.6 Hz, H-α), 3.29 (1H, *t*, *J* = 7.6 Hz, H-β), 6.72 (3H, *m*, H-2,5,6), 7.21 (1H, *dd*, *J* = 8.8, 1.0 Hz, H-5′), 7.66 (1H, *d*, *J* = 8.8 Hz, H-6′), 7.61 (1H, *d*, *J* = 2.1 Hz, H-2″), 6.99 (1H, *dd*, *J* = 2.1, 1.0 Hz, H-3″), 5.91 (2H, *s*, H-2‴), 4.13 (3H, *s*, 2′-OMe). ^{13}C NMR: see Table 1. EIMS *m/z* (rel. int.): 324 (13), 293 (4), 175 (100), 160 (25), 148 (28), 135 (23).

6-Methoxy-6″,6″-dimethylchromeno-[2″,3″:7,8]-flavanone (**4a**). ^{1}H NMR: 5.46 (1H, *dd*, *J* = 13.1, 3.1 Hz, H-2), 3.02 (1H, *dd*, *J* = 16.8, 13.1 Hz.H-3ax), 2.84 (1H, *dd*, *J* = 16.8, 3.1 Hz, H-3eq), 7.28 (1H, *s*, H-5), 7.39 (5H, *m*, H-2′,-6′), 5.60 (1H, *d*, *J* = 9.9 Hz, H-3″), 6.65 (1H, *d*, *J* = 9.9 Hz, H-4″), 1.58 (6H, *s*, 2″-Me_2), 3.87 (3H, *s*, 6-OMe). ^{13}C NMR: see Table 3. EIMS *m/z* (rel. int.): 336 (36), 321 (100), 217 (80), 189 (5), 174 (5), 77 (9).

(2S)-5,6-Dimethoxy-[2″,3″:7,8]-furanoflavanone (**4b**). ^{1}H NMR: 5.56 (1H, *dd*, *J* = 13.1, 2.9 Hz, H-2), 3.13 (1H, *dd*, *J* = 16.5, 13.1 Hz, H-3ax), 2.90 (1H, *dd*, *J* = 16.5, 2.9 Hz, H-3eq), (5H, *m*, H-2′-6′), 7.59 (1H, *d*, *J* = 2.2 Hz, H-2″), 6.90 (1H, *d*, *J* = 2.2 Hz, H-3″), 3.97, 4.07 (2 × 3H, 2 × *s*, 5-OMe, 6-OMe). ORD: $[\phi]_{372}$ + 528.8; $[\phi]_{361}$0; $[\phi]_{340}$ − 1876.1.

(2S)-3′,4′-Methylenedioxy-6″,6″-dimethylchromeno-[2″,3″:7,8]-flavanone (**4c**). UV λ_{max} nm (log ε): 270 (4.41). IR ν_{max} cm^{-1} (KBr): 2922, 1681, 1490, 1376, 1330, 1034, 816. ^{1}H NMR: 5.37 (1H, *dd*, *J* = 13.0, 3.0 Hz, H-2), 2.98 (1H, *dd*, *J* = 16.8, 13.0 Hz, H-3ax), 2.79 (1H, *dd*, *J* = 16.8, 3.0 Hz, H-3eq), 7.74 (1H, *d*, *J* = 8.4 Hz, H-5), 6.50 (1H, *d*, *J* = 8.4 Hz, H-6), 6.99 (1H, *d*, *J* = 1.6 Hz, H-2′), 6.91 (1H, *dd*, *J* = 7.9, 1.6 Hz, H-6′), 6.84 (1H, *d*, *J* = 7.9 Hz, H-5′), 5.57 (1H, *d*, *J* = 10.0 Hz, H-3″), 6.63 (1H, *d*, *J* = 10.0 Hz, H-4″), 1.44, 1.47 (2 × 3H, 2 × *s*, 2″-Me_2), 6.00 (2H, *s*, H-2‴). ^{13}C NMR: 79.7 (C-2), 44.3 (C-3), 190.6 (C-4), 127.9 (C-5), 115.9 (C-6), 159.6 (C-7), 109.4 (C-8), 157.6 (C-9), 114.7 (C-10), 132.8 (C-1′), 106.7 (C-2′), 148.0 (C-3′), 147.8 (C-4′), 108.3 (C-5′), 119.8 (C-6′), 77.5 (C-2″), 128.9 (C-3″), 111.2 (C-4″), 101.3 (C-2‴), 28.4, 28.1 (2″-OMe). EIMS *m/z* (rel. int.): 350 (7), 335 (14), 187 (100), 148 (19). ORD: $[\phi]_{356}$ + 755.5; $[\phi]_{346}$ 0; $[\phi]_{327}$ − 5080.2.

(2S)-3′,4′-Dimethoxy-6″,6″-dimethylchromeno-[2″,3″:7,8]-flavanone (**4d**). UV λ_{max} nm (log ε): 271 (4.39), 311–303 (3.75). IR ν_{max} cm^{-1} (KBr): 2957, 1681, 1595, 1259, 1097, 1027. ^{1}H NMR: 5.42 (1H, *dd*, *J* = 12.9, 3.0 Hz, H-2), 3.04 (1H, *dd*, *J* = 16.8, 12.9 Hz, H-3ax), 2.82 (1H, *dd*, *J* = 16.8, 3.0 Hz, H-3eq), 7.74 (1H, *d*, *J* = 8.7 Hz, H-5), 6.50 (1H, *d*, *J* = 8.7 Hz, H-6), 7.08 (2H, *m*, H-2′,6′), 6.91 (1H, *d*, *J* = 9.0 Hz, H-5′), 6.57 (1H, *d*, *J* = 10.0 Hz, H-3″), 6.64 (1H, *d*, *J* = 10.0 Hz, H-4″), 1.44, 1.47 (2 × 3H, 2 × *s*, 2″-Me_2), 3.91, 3.92 (2 × 3H, 2 × *s*, 3′-OMe, 4′-OMe). ^{13}C NMR: 79.8 (C-2), 44.3 (C-3), 190.7 (C-4), 127.9 (C-5), 115.9 (C-6), 159.6 (C-7), 109.4 (C-8), 157.6 (C-9), 114.8 (C-10), 131.5 (C-1′), 109.4 (C-2′), 149.3, 149.2 (C-3′, C-4′), 111.1 (C-5′), 118.7 (C-6′), 77.5 (C-2″), 128.9 (C-3″), 111.2 (C-4″), 28.4, 28.1 (2″-OMe), 56.0 (3′-OMe, 4′-OMe). EIMS *m/z* (rel. int.): 351 (160), 187 (100), 164 (28), 149 (9). ORD: $[\phi]_{355}$ + 5112.1; $[\phi]_{343}$ 0; $[\phi]_{337}$ − 4376.5.

(2R,3R)-3,5,6-Trimethoxy-[2″,3″,7,8]-furanoflavanonol (**5**). UV λ_{max} nm (log ε): 340 (3.31), 252 (4.26). *IR* ν_{max} cm^{-1} (KBr): 2920, 1700, 1610, 1470, 1120, 1060. ^{1}H NMR: 5.44 (1H, *d*, *J* = 9.6 Hz, H-2), 4.09 (1H, *d*, *J* = 9.6 Hz, H-3), 7.45 (5H, *m*, H-2′-6′), 7.58 (1H, *d*, *J* = 2.2 Hz, H-2″), 6.87 (1H, *d*, *J* = 2.2 Hz, H-3″), 3.44 (3H, *s*, 3-OMe), 3.97, 4.07 (2 × 3H, 2 × *s*, 5-OMe, 6-OMe). ^{13}C NMR: see Table 3. EIMS *m/z*

(rel. int.): 354 (5), 220 (100), 205 (98), 177 (12), 134 (16), 91 (30), 77 (14). ORD: $[\phi]_{375}$ + 2075.5; $[\phi]_{355}$ 0; $[\phi]_{338}$ − 4122.4.

(2,4 - cis) - 3′,4′ - *Methylenedioxy* - 4,5,8 - *trimethoxy* - [2″,3″:7,6] - *furanoflavan* (**6a**). Oil. UV λ_{max} nm (log ε): 240 (4.15), 267 (4.11). IR ν_{max} cm^{-1} (KBr): 2910, 1620, 1480, 1440, 1350, 1150, 1150, 1050. ^{1}H NMR: see Table 4; ^{13}C NMR: see Table 3. EIMS *m/z* (rel. int.): 384 (54), 352 (46), 349 (31), 289 (38), 236 (100), 221 (61), 193 (8), 149 (15), 148 (8). ORD: $[\phi]_{296}$ − 734.5; $[\phi]_{302}$ 0; $[\phi]_{272}$ + 1441.6.

(2,4-cis)-4,5,6-*Trimethoxy*-[2″,3″:7,8]-*furanoflavan* (**6b**). ^{1}H NMR: see Table 4; ^{13}C NMR: see Table 3.

(2,3 - trans - 3,4 - trans) - 3,4,5,8 - *Tetramethoxy* - [2″,3″:7,6] - *furanoflavan* (**6c**). Mp: 113.9°. UV λ_{max} nm (log ε): 239 (3.96), 262 (4.08). IR ν_{max} cm^{-1} (film): 2920, 1480, 1130, 1100. ^{1}H NMR: 5.03 (1H, *d*, *J* = 6.6 Hz, H-2), 3.90 (1H, *dd*, *J* = 6.6, 4.3 Hz, H-3), 4.79 (1H, *d*, *J* = 4.3 Hz, H-4), 7.47 (2H, *br d*, *J* = 8.0 Hz, H-2′, 6′), 7.34 (3H, *m*, H-3′–5′), 7.50 (1H, *d*, *J* = 2.2 Hz, H-2″), 6.86 (1H, *d*, *J* = 2.2 Hz, H-3″), 3.28 (3H, *s*, 3-OMe), 3.35 (3H, *s*, 4-OMe), 4.06 (3H, *s*, 5-OMe), 4.04 (3H, *s*, 8-OMe). ^{13}C NMR: see Table 3. EIMS *m/z* (rel. int.): 370 (20), 236 (80), 221 (100), 193 (20), 134 (20), 105 (10), 91 (70), 77 (70). ORD: $[\phi]_{295}$ − 1941.9; $[\phi]_{280}$ 0; $[\phi]_{274}$ + 900.1.

(2,3-trans-3,4-cis)-3,4,5,6-*Tetramethoxy*-[2″,3″:7,8]-*furanoflavan* (**6d**). UV λ_{max} nm (log ε): 258 (4.33). IR ν_{max} cm^{-1} (film): 2918, 1482, 1280, 1100, 1065. ^{1}H NMR: 5.15 (1H, *d*, *J* = 6.5 Hz, H-2), 3.91 (1H, *dd*, *J* = 6.5, 4.7 Hz, H-3), 4.66 (1H, *d*, *J* = 4.7 Hz, H-4), 7.39 (5H, *m*, H-2′-6′), 7.51 (1H, *d*, *J* = 2.2 Hz, H-2″), 6.82 (1H, *d*, *J* = 2.2 Hz, H-3″), 3.28 (3H, *s*, 3-OMe), 3.38 (3H, *s*, 4-OMe), 3.98, 4.07 (2 × 3H, 2 × *s*, 5-OMe, 6-OMe-0. ^{13}C NMR: see Table 3. EIMS *m/z* (rel. int.): 370 (12), 236 (72), 221 (100), 193 (12), 134 (9). ORD: $[\phi]_{304}$ − 306.6; $[\phi]_{295}$ 0; $[\phi]_{27}$ + 1562.7.

(2,3-trans-3,4-trans)-3′,4′-*Methylenedioxy*-3,4,5,8-*tetramethoxy* - [2″,3″:7,6] - *furanoflavan* (**6e**). Mp: 106.5°. UV λ_{max} nm (log ε): 256 (4.34). IR ν_{max} cm^{-1} (KBr): 2920, 1470, 1430, 1350, 1120, 1090, 1050. ^{1}H NMR: see Table 4; ^{13}C NMR: see Table 3. EIMS *m/z* (rel. int.): 414 (36), 326 (6), 236 (100), 221 (54), 193 (6), 178 (12), 165 (14), 149 (3), 135 (8), 133 (8). ORD: $[\phi]_{297}$ − 739.9; $[\phi]_{283}$ 0; $[\phi]_{276}$ + 1010.4.

(2,3 - trans - 3,4 - cis) - 3′,4′ - *Methylenedioxy* - 3,4,5,6-*tetramethoxy*-[2″,3″:7,8]-*furanoflavan* (**6f**). UV λ_{max} nm (log ε): 262 (4.23), 242 (4.27). IR ν_{max} cm^{-1} (KBr): 2936, 1625, 1489, 1444, 1354, 1251, 1136, 737. ^{1}H NMR: see Table 4; ^{13}C NMR: see Table 3. EIMS *m/z* (rel. int.): 414 (36), 236 (100), 221 (54), 193 (6), 178 (12), 165 (14), 149 (3), 135 (8). ORD: $[\phi]_{302}$ − 3635.0; $[\phi]_{287}$ 0; $[\phi]_{270}$ + 9253.0.

6″,6″ - *Dimethylchromene* - [2″, 3″:7,8] - *flavone* (**7a**). Mp: 137.0°. UV λ_{max} nm (log ε): 241 (4.44), 271 (4.53), 324 (4.10). IR ν_{max} cm^{-1} (KBr): 1650, 1580, 1450, 1400, 1370, 1120, 1090. ^{1}H NMR: 6.76 (1H, *s*, H-3), 7.99 (1H, *d*, *J* = 8.8 H-5), 6.86 (1H, *d*, *J* = 8.8 Hz, H-6), 7.90 (2H, *m*, H-2′,6′), 7.54 (3H, *m*, H-3′-5′), 5.76 (1H, *d*, *J* = 10.0 Hz, H-3″), 6.94 (1H, *d*, *J* = 10.0 Hz, H-4″), 1.52 (6H, *s*, 2″-Me_2). ^{13}C NMR: 162.9 (C-2), 107.6 (C-3), 178.3 (C-4), 126.3 (C-5), 115.4 (C-6), 157.8 (C-7), 109.7 (C-8), 152.6 (C-9), 118.0 (C-10), 132.4 (C-1′), 126.3 (C-2′), 129.3 (C-3′), 130.7, 131.7 (C-4′, C-3″), 129.3 (C-5′), 126.3 (C-6′), 77.9 (C-2″), 115.4 (C-4″), 28.2 (2″-Me). EIMS *m/z* (rel. int.): 304 (71), 290 (71), 289 (100), 187 (86), 202 (6), 159 (18), 145 (41), 131 (26), 115 (12), 105 (12), 102 (31), 77 (54).

3′,4′ - *Methylenedioxy* - 6″,6″ - *dimethylchromeno* - [2″,3″:7,8] - *flavone* (**7b**). Mp: 231.9°. UV λ_{max} nm (log ε): 241 (4.72), 273 (4.49), 330 (4.53). IR ν_{max} cm^{-1} (KBr): 1638, 1585, 1502, 1448, 1391, 1378, 1291, 1030. ^{1}H NMR: 6.62 (1H, *s*, H-3), 7.97 (1H, *d*, *J* = 8.7 Hz, H-5), 6.84 (1H, *d*, *J* = 8.7 Hz, H-6), 7.31 (1H, *d*, *J* = 1.8 Hz, H-2′), 7.45 (1H, *dd*, *J* = 8.3, 1.8 Hz, H-6′), 6.93 (1H, *d*, *J* = 8.3 Hz, H-5′), 5.75 (1H, *d*, *J* = 10.5 Hz, H-3″), 6.89 (1H, *d*, *J* = 10.5 Hz, H-4″), 6.07 (2H, *s*, H-2‴), 1.51 (6H, *s*, 2″-Me_2). ^{13}C NMR: 162.2 (C-2), 108.8 (C-3), 177.8 (C-4), 126.0 (C-5), 115.2, 115.0 (C-6, C-4″), 157.5 (C-7), 109.4 (C-8), 152.2 (C-9), 117.7 (C-10), 125.9 (C-1′), 106.4 (C-2′), 148.5 (C-3′), 150.5 (C-4′), 106.1 (C-5′), 121.2 (C-6′), 77.7 (C-2″), 130.5 (C-3″), 101.9 (C-2‴), 28.1 (2″-Me_2). EIMS *m/z* (rel. int.): 348 (17), 333 (97), 187 (100), 166 (28), 145 (14), 131 (14), 103 (10), 77 (23).

3′,4′ - *Methylenedioxy* - 8 - *methoxy* - 5 - *hydroxy* - 6″,6″ - *dimethylchromeno* - [2″,3″:7,6] - *isoflavone* (**8**). ^{1}H NMR: 7.73 (1H, s, H-2), 7.12 (1H, *d*, *J* = 1.6 Hz, H-2′), 6.84 (1H, *d*, *J* = 7.9 Hz, H-5′), 7.09 (1H, *dd*, *J* = 7.9 and 1.6 Hz, H-6′), 5.47 (1H, *d*, *J* = 9.9 Hz, H-3″), 6.69 (1H, *d*, *J* = 9.9 Hz, H-4″), 1.56 (6H, *s*, 2″-Me_2), 6.03 (2H, *s*, H-2‴), 3.92 (3H, *s*, 8-OMe), 14.60 (1H, *s*, 5-OH).

(6*aβ*,12*aβ*) - 12*a* - *Hydroxy* - 4′,5′ - *tetrahydro* - 2,3 - *dimethyoxy* - 5′ - *isopropenylfuran* - [2′,3′:9,8] - 6*H* - *rotoxen* - 12 - *one* (**9**). ^{1}H NMR: 6.55 (1H, *s*, H-1), 6.48 (1H, *s*, H-4), 4.49 (1H, *dd*, *J* = 13.1, 2.3 Hz, H-6), 4.59 (3H, *m*, H-6a, 6, OH), 6.53 (1H, *d*, *J* = 8.6 Hz, H-10), 7.83 (1H, *d*, *J* = 8.6 Hz, H-11), 2.93 (1H, *dd*, *J* = 16.0, 9.0 Hz, H-4′a), 3.29 (1H, *dd*, *J* = 16.0, 9.0 Hz, H-4′b), 5.24 (1H, *t*, *J* = 9.0 Hz, H-5′), 5.07 (1H, *s*, H-7′a), 4.94 (1H, *s*, H-7′b), 1.76 (3H, *s*, H-8′), 3.82, 3.72 (2 × 3H,2 × *s*, 2-OMe, 3-OMe). ^{13}C NMR: 109.5 (C-1), 108.9 (C-1a), 143.1 (C-2), 151.4 (H-3), 101.2 (C-4), 148.6 (C-4a), 63.9 (C-6), 76.2 (C-6a), 157.9 (C-7a), 113.4 (C-8), 168.3 (C-9), 105.5 (C-10), 130.3 (C-11), 111.9 (C-11a), 191.4 (C-12), 67.7 (C-12a), 31.2 (C-4′), 88.1 (C-5′), 143.1 (C-6′), 112.9 (C-7′), 17.1 (C-8′), 56.0, 56.5 (2-OMe, 3-OMe).

(*E*) - 2′ - *Methoxy* - 6″,6″ - *dimethylchromeno* - [2″, 3″: 4′,3′]-9-*methoxychalcone* (**1e**). ^{1}H NMR: 7.82 (2H, H-2,6), 7.34 (3H, H-3,4,5), 6.27 (1H, H-8), 6.52 (1H, H-5′), 6.98 (1H, H-6′), 5.57 (1H, H-3″), 6.53 (1H, H-4″), 3.71 (3H, 9-OMe), 3.89 (3H, 2′-OMe), 1.40 (6H, 2″-Me_2). ^{13}C NMR: 128.0 (C-1), 128.0 (C-2,6), 128.1 (C-3,5), 131.7 (C-4), 169.2 (C-7), 99.7 (C-8), 139.6 (C-9), 121.4 (C-1′), 154.0 (C-2′), 114.5 (C-3′), 155.2 (C-4′), 111.9 (C-5′), 129.9 (C-6′), 76.6 (C-2″), 130.1 (C-3″), 116.8 (C-4″), 56.2 (9-OMe), 61.9 (2′-OMe), 29.5 (2′-Me_2).

(*Z*) - 2′ - *Methoxy* - 6″,6″ - *dimethylchromeno* - [2″,3″: 4′,3′]-7-*methoxychalcone* (**12**). ^{1}H NMR: 7.64 (2H,

H-2,6), 7.41 (3H, H-3,4,5), 6.55 (1H, H-8), 6.62 (1H, H-5′), 7.56 (1H, H-6′), 5.67 (1H, H-3″), 6.63 (1H, H-4″), 3.79 (3H, 7-OMe), 3.91 (3H, 2′-OMe), 1.45 (6H, 2″-Me_2). ^{13}C NMR: 128.9 (C-1), 127.7 (C-2,6), 128.5 (C-3,5), 131.2 (C-4), 167.8 (C-7), 107.4 (C-8), 135.8 (C-9), 127.1 (C-1′), 155.8 (C-2′), 114.7 (C-3′), 157.1 (C-4′), 112.5 (C-5′), 130.4 (C-6′), 76.6 (C-2″), 130.5 (C-3″), 116.6 (C-4″), 61.0 (7-OMe), 63.2 (2′-OMe), 27.9 (2′-Me_2).

(*E*) - 2′ - *Methoxy* - 6″,6″ - *dimethylchromeno* - [2″,3″: 4′,3′]-7-*methoxychalcone* (**12**). ^{1}H NMR: 7.44 (2H, H-2,6), 7.32 (3H, H-3,4,5), 6.34 (1H, H-8), 6.52 (1H, H-5′), 7.41 (1H, H-6′), 5.65 (1H, H-3″), 6.58 (1H, H-4″), 3.82 (3H, 7-OMe), 3.88 (3H, 2′-OMe), 1.42 (6H, 2″-Me_2). ^{13}C NMR: 130.6 (C-1), 127.9 (C-2,6), 129.1 (C-3,5), 131.4 (C-4), 171.1 (C-7), 102.4 (C-8), 135.7 (C-9), 127.3 (C-1′), 155.8 (C-2′), 114.8 (C-3′), 157.1 (C-4′), 112.6 (C-5′), 129.9 (C-6′), 76.7 (C-2″), 130.6 (C-3″), 116.8 (C-4″), 56.6 (7-OMe), 63.5 (2′-OMe), 28.0 (2′-Me_2).

(2,4 - cis) - 4 - *Hydroxy* - 5,6 - *dimethoxy* - [2″,3″: 7,8] - *furanoflavan* (**16**). ^{1}H NMR: 5.23 (1H, *dd*, J = 12.1, 1.6 Hz, H-2), 2.13 (1H, *m*, H-3ax), 2.36 (1H, *dt*, J = 15.0, 1.6 Hz, H-3eq), 5.06 (1H, *dd*, J = 3.4, 1.6 Hz, H-4), 7.35–7.53 (6H, *m*, H-2′–6′,2″), 6.84 (1H, *d*, J = 2.1 Hz, H-3″), 4.08, 4.07 (2 × 3H, 2 × *s*, 5-OMe, 6-OMe). ^{13}C NMR: 73.7 (C-2), 38.2 (C-3), 60.4 (C-4), 148.0 (C-5), 132.8 (C-6), 148.8 (C-7), 115.0 (C-8), 144.0 (C-9), 112.5 (C-10), 141.6 (C-1′), 126.8 (C-2′,6′), 129.0 (C-3′,5′). 128.5 (C-4′), 144.3 (C-2″), 104.9 (C-3″), 61.3, 61.9 (5-OMe, 6-OMe).

(2,4 - trans) - 4 - *Hydroxy* - 5,6 - *dimethoxy* - [2″,3″: 7,8] - *furanoflavan* (**17**). ^{1}H NMR: 5.50 (1H, *dd*, J = 11.7, 1.8 Hz, H-2), 1.97–2.07 (1H, *m*, H-3ax), 2.82 (1H, *dt*, J = 13.8, 2.1 Hz, H-3eq), 4.97 (1H, *t*, J = 2.4 Hz, H-4), 7.4–7.7 (6H, *m*, H-2′-6′,2″) 6.80 (1H, *d*, J = 2.1 Hz, H-3″) 3.91, 4.05 (2 × 3H, 2 × *s*, 5-OMe, 6-OMe). ^{13}C NMR: 74.0 (C-2), 34.6 (C-3), 64.6 (C-4), 149.3 (C-5), 142.4 (C-6), 148.7 (C-7), 114.8 (C-8), 145.2 (C-9), 112.2 (C-10), 142.3 (C-1′), 127.0 (C-2′,6′), 128.7 (C-3′,5′), 128.2 (C-4′), 144.0 (C-2″), 104.9 (C-3″), 61.4, 61.3 (5-OMe, 6-OMe).

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