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FURTHER 5-METHYL COUMARINS AND OTHER CONSTITUENTS FROM THE SUBTRIBE MUTISIINAE

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Key Word Index—*Mutisia spinosa, M. retrorsa; Trichocline sinuata; Brachyclados megalanthus*; Compositae; chemotaxonomy; 5-methyl coumarins; monoterpenes; geraniol and linalol derivatives; C_{14}-acetylenic compound.

Abstract—The investigation of four species from the subtribe Mutisiinae afforded eight new monoterpenes, seven 5-methyl coumarins, two closely related 5-methyl chromones, two coumarane derivatives, a *p*-hydroxy acetophenone derivative and a new C_{14}-acetylene. The structures were elucidated by spectroscopic methods and a few chemical transformations. The chemotaxonomy of the Mutisiinae is discussed.

INTRODUCTION

The tribe Mutisieae (Compositae) is divided into four subtribes [1]. Chemical investigations of representatives of these subtribes have shown that, at least in part, the proposed relationships are supported by special types of constituents. We have now investigated four species belonging to the subtribe Mutisiinae; the results are discussed in the present paper.

RESULTS AND DISCUSSION

The aerial parts of *Mutisia spinosa* afforded in addition to known compounds (see Experimental) several new ones related to geranyl or linalyl acetate (**1**–**6**, **8** and **9**) as well as the 5-methyl coumarin derivative **10** and two closely related coumaranes (**11** and **12**). The roots gave trideca-pentaynene and trideca-1,11-dien-3,5,7,9-tetrayne, several widespread compounds piloselloidan (**13**) [2], the corresponding farnesyl derivative **14** and the related chromone derivative **17**.

The structure of **1** followed from the ^{1}H NMR spectrum (Table 1). Spin decoupling allowed the assignment of the whole sequence. The couplings and the chemical shifts further showed that a primary acetoxy and a secondary hydroxy group were present. The structure was elucidated by mass spectrometry although no molecular ion could be detected. However, ion *m/z* 152 obviously was formed by loss of acetic acid as high resolution indicated that this fragment had only one oxygen ($C_{10}H_{16}O$). The ^{1}H NMR spectrum of **2** (Table 1) only differed from that of **1** by small downfield shifts of the H-6 and H-9 signals and the presence of a typical hydroperoxide singlet at δ7.90. The presence of the hydroperoxide related to **1** was confirmed by reduction with triphenyl phosphine which afforded the carbinol **1**.

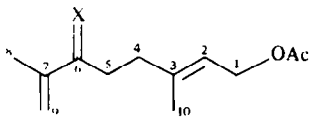
The ^{1}H NMR spectrum of **3** (Table 1) indicated that again a primary allylic acetate was present. However, the IR spectrum indicated a conjugated ketone (1680, 1630 cm^{-1}). A downfield triplet at δ2.81 and the chemical shift of the H-9 signal as well as spin decoupling established the structure **3** for this compound.

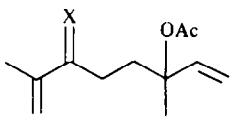
The ^{1}H NMR spectrum of **4** (Table 1) was different from those of **1** and **2**. The singlet at δ7.87 showed that again a hydroperoxide was present. However, the absence of a 2,3-double bond clearly followed from a pair of doublets of triplets at δ4.12 and 4.06 as well as from the methyl doublet at δ0.90. In the mass spectrum the highest fragment (*m/z* 197) was formed by loss of OOH as in the spectrum of **2** where the corresponding fragment was *m/z* 195 ($C_{12}H_{19}O_2$).

The ^{1}H NMR spectra of **5** and **6** (Table 1) clearly showed that we were dealing with isomers of **1** and **2**, respectively, where the acetate group was now tertiary. Again a singlet at δ7.99 clearly showed that **6** was a hydroperoxide. Accordingly, **6** was transformed by heating with acetic anhydride to the ketone **7**, its ^{1}H NMR spectrum (Table 1) was in part similar to those of **3** and **6**.

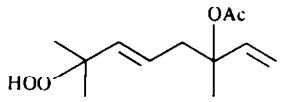
The ^{1}H NMR spectra of **8** and **9** (Table 1) clearly showed that again hydroperoxides were present with 5*E*-double bonds differing in the position of the second double bond and the acetoxy group. Most likely for these monoterpenes geranyl and linalyl acetate, respectively, and for **4** the corresponding 2,3-dihydrogeranyl acetate, are the precursors. As the nonpolar fractions only gave geranyl acetate it is not very likely that these compounds are artifacts.

The ^{1}H NMR spectrum of **10** (Table 2) showed some similarities to those of a group of characteristic 5-methyl coumarins which have been isolated from different genera of the tribe Mutisieae [2–11] but also from a few genera of the tribe Vernonieae [12–18]. Especially the group of signals of aromatic protons together with a broadened methyl singlet at δ2.68 were typical. As the molecular formula was $C_{20}H_{24}O_4$ it was very likely that the 4-hydroxy-5-methyl coumarin part was combined in some way with a monoterpene moiety. Accordingly, the signals of the sequence $CH_2CH_2CH{=}CMe_2$ were present. A second sequence included a tertiary proton at an oxygen bearing carbon which was coupled with two protons displaying a pair of double doublets at δ3.15 and 3.08. A methyl singlet at δ1.35 and a hydroxy group, which was deduced from the corresponding IR band, led to the





1 X = H,OH **2** X = H,OOH **5** X = H,OH **6** X = H,OOH
3 X = O **4** X = H,OOH(2,3H) **7** X = O



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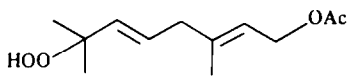

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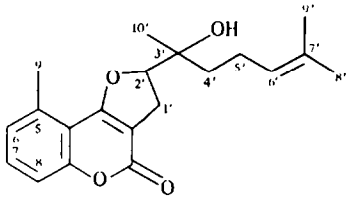

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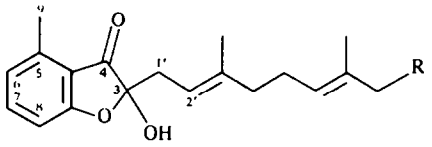
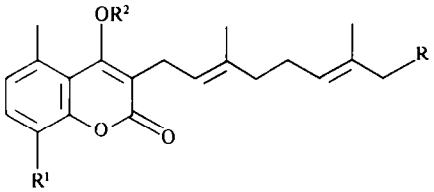
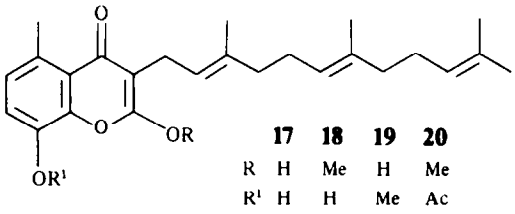


11 R = H
12 R = $CH_2CH=C(Me^{15'})(Me^{14'})$



	13	14	15	16
R	H	$CH_2CH=CMe_2$		
R^1	H	H	OAc	OAc
R^2	H	H	H	Me



	17	18	19	20
R	H	Me	H	Me
R^1	H	H	Me	Ac

proposed structure. The strong fragment *m/z* 201 supported this suggestion as *m/z* 201 most likely was formed by fission of the 2',3'-bond. The relative configurations at C-2' and C-3' were not determined.

The ^{1}H NMR spectra of **11** and **12** (Table 2), which differed in the molecular formulae by an isoprene unit, indicated that again trisubstituted aromatic compounds were present. The chemical shifts of the aromatic protons were shifted upfield when compared with those of **10** and related 5-methyl coumarins, but were close to those of 6-methyl salicylic acid which also was present in this species. All signals of the spectra of **11** and **12** could be assigned by spin decoupling leading to sequences with a geranyl and a farnesyl residue for **11** and **12**, respectively. A strong fragment *m/z* 164 ($C_9H_8O_3$) most likely was formed by a McLafferty fragmentation. All data and a hydroxy band in the IR spectra of **11** and **12** led to the proposed structures. Compound **11** most likely is derived from piloselloidan (**13**) [2] by hydrolysis of the lactone followed by oxidative decarboxylation. The resulting diketone would directly lead to the semi-acetal. Coumarin **13** was isolated from the roots together with the corresponding farnesyl derivative **14** which could be the precursor of **12**. The structure of **14** could be easily deduced from the ^{1}H NMR spectrum (Table 2) as it was very close to that of **13**. The structure of the main constituent **17** followed from the spectral data and those of some derivatives. The ^{1}H NMR spectrum of **17** (Table 2), which had one more oxygen than **14**, differed from that of the latter by the signals of the aromatic

Table 1. ^{1}H NMR spectral data of **1–9** (400 MHz, $CDCl_3$, TMS as int. standard)

	1	2	3	4	5	6	7	8	9
H-1	4.58 *br d*	4.58 *br d*	4.58 *br d*	4.12 *dt* 4.06 *dt*	5.14 *d* (*t*) 5.12 *d* (*c*)	5.13 *d* (*t*) 5.11 *d* (*c*)	5.15 *d* (*t*) 5.14 *d* (*c*)	5.15 *d* (*t*) 5.14 *d* (*c*)	4.56 *br d*
H-2	5.37 *tq*	5.36 *tq*	5.34 *tq*		5.94 *dd*	5.91, 5.90 *dd*	5.93 *dd*	5.98 *dd*	5.34 *tq*
H-4	2.14 *m*	2.08 *m*	2.35 *br t*		2.10 *m*	1.92 *m* 1.70 *m*	2.18 *m* 2.04 *m*	2.62 *dd* 2.58 *dd*	2.74 *br d*
H-5	1.67 *m*	1.58 *m*	2.81 *t*	1.62 *m*	1.68 *m*	1.58 *m* 1.81 *m*	2.70 ABX_2	5.64 *dt*	5.64 *dt*
H-6	4.04 *br t*	4.28 *t*	—	4.28 *t*	4.04 *br t*	4.26 *t*	—	5.59 *d*	5.57 *d*
H-8	1.71 *br s*	1.79 *br s*	1.87 *br s*	1.74 *br s*	1.71 *br s*	1.70 *br s*	1.87 *br s*	1.32 *s*	1.31 *s*
H-9	4.95 *br s*	5.03 *dq*	5.97 *br s*	5.02 *dq*	4.93 *br s*	5.02 *q*	5.95 *br s*		
H-9	4.85 *br s*	5.01 *q*	5.78 *q*	5.00 *br s*	4.84 *br s*	5.00 *br s*	5.77 *q*		
H-10	1.72 *br s*	1.69 *br s*	1.72 *br s*	0.90 *d*	1.54 *s*	1.51, 1.50 *s*	1.56 *s*	1.51 *s*	1.66 *br s*
OAc	2.05 s	2.04 s	2.05 s	2.05 s	2.01 s	1.99 s	2.00 s	1.99 s	2.03 s
OOH	—	7.90 *s*	—	7.87 *s*	—	7.99 *s*	—	7.38 *s*	7.68 *s*

J (Hz): Compounds **1–3** and **9**: 1,2 = 7.5; 5,6 = 6.5; 2,4 = 2,10 = 1 (compound **3**: 4,5 = 7.5; 8,9 = 1; compound **9**: 4,5 = 6; 5,6 = 16); compound **4**: 1,1′ = 11; 1,2 = 3,10 = 7; 5,6 = 6.5; 6,9 = 8,9 ~ 1.5; compounds **5–8**: 1t, 2 = 17; 1c,2 = 11; 5,6 = 6.5; 8,9 ~ 1; (compound **8**: 4,4′ = 16; 4,5 = 5).

protons. In the spectrum of **17** a pair of doublets indicated an additional substituent at C-6 or C-8 while all the other signals were nearly identical to the spectra of **14** and **17**. However, the IR spectrum of **17** displayed a typical band for a cross conjugated keto group typical for γ-chromones as well as a hydroxy band. The allylic coupling of H-9 required a 8-hydroxy group. Partial acetylation of **17** gave the monoacetate **15** as could be deduced from the spectral data. Especially the IR band was shifted to 1730 cm^{-1} indicating the presence of a coumarin. The monoacetate **15** gave by addition of diazomethane the corresponding methyl ether **16** and the isomeric chromone **20** as again could be deduced from the IR bands. Similarly **17** could be transformed by reaction with diazomethane to a mixture of **18** and **19**. As in related compounds the methoxy signal in the spectrum of **18** was at lower fields as in that of **19** while the IR bands indicated that both compounds were chromones.

The aerial parts of *Mutisia retrorsa* gave widespread compounds (see Experimental) and a methyl ester with a UV spectrum typical of an enediyne diene [19]. The ^{1}H NMR spectrum (see Experimental) indicated the presence of the C_{14}-acetylenic ester **29**. As all signals could be assigned by spin decoupling the structure directly followed from the ^{1}H NMR spectral data. Acetylenes are not very common in the tribe. As no roots of this species were available it is not known whether this part of this species also contain the typical 5-methyl coumarins or related compounds.

From the aerial parts of *Trichocline incana* three furocoumarins were isolated [20]. We now have studied the constituents of a further species, *T. sinuata*. The aerial parts also gave eight known furocoumarins in addition to widespread compounds (see Experimental). Most of the coumarins were also present in the roots.

The aerial parts of *Brachyclados megalanthus* also gave the furocoumarins imperatorin, isoimperatorin, 7-isopentenyloxy coumarin, bergapten and oxypeudedanin as well as the isovaleroyl phenol **27**. The corresponding ketone **28** was isolated previously [21]. The structure of **27** followed from the spectral data and was established by manganese dioxide oxidation of **27** which afforded **28**. The roots gave bergapten, psoralene and **27**. Furthermore, a complex mixture was obtained which only could be separated by a combination of different techniques. Finally 6-acetyl-2,2-dimethyl chromene (**28**) and four 5-methyl coumarins (**21–24**) as well as the isomeric chromone **26** and the *nor*-derivative **25** were obtained.

The structure of **21** followed from the molecular formula and the ^{1}H NMR spectrum (Table 2). The presence of a 5-methyl-4-hydroxycoumarin derivative was deduced from the typical ^{1}H NMR signals while the nature of the side chain followed from the chemical shifts, the couplings and spin decoupling. The broadened quartet at δ3.88 showed couplings with the methyl group (H-1′), with H-4′ and H-5′ (homoallylic). Irradiation at the centre of a pair of double doublets (2.88) collapsed both signals at 5.75 and 5.16 to broadened singlets. Since the latter was coupled with two olefinic methyls and the former was only coupled with one olefinic methyl, the whole sequence of the side chain was established. In the mass spectrum of **21** the observed fragments most likely were the results of double bond migration. Thus a migration of the 3′,4′-double bond into conjugation with the 6′,7′-double bond would lead to a preferred formation of *m/z* 203 $[M - C_8H_{13}]^+$ while the migration of the same double bond in conjugation to the coumarin would prefer a loss of C_6H_{10} and C_6H_{11}.

The structures of the epimeric coumarins **22** and **23** also followed from the ^{1}H NMR spectra (Table 2). The presence of 5-methyl coumarins could be deduced from the typical signals. The nature of the side chain was determined by spin decoupling and from the chemical shift of the H-2′ signal which required a position on an oxygen bearing carbon. The mass spectra further supported the proposed branching at C-3′ by the strong fragments *m/z* 230 and 229 $[M - C_6H_{10}$ or $C_6H_{11}]^+$. The relative stereochemistry at C-2′ and C-3′ was determined by NOE difference spectroscopy. Thus **22** showed a clear NOE between H-1′ and H-10′ and a weak one with H-9 which itself showed an NOE with H-6. In the case of **23** a strong NOE between H-10′ and H-2′ was visible while no effect was observed between H-1′ and H-10′. The absolute configuration was not determined. However, **22** showed a

Table 2. ^{1}H NMR spectral data of **10**–**12** and **14**–**26** (400 MHz, $CDCl_3$, TMS as int. stanard)

	10	**11**	**12***	**14***	**15*†**	**16*‡**	**17***	**18*§**	**19*‖**	**20*¶**	**21****	**22**	**23**	**24**	**25††**	**26**
H-6	7.04 *br d*	6.85 *br d*	6.84 *br d*	7.02 *br d*	7.18 *br d*	7.21 *br d*	7.06 *br d*	7.11 *br d*	7.08 *br d*	7.24 *br d*	7.01 *br d*	7.01 *br d*	7.01 *br d*	7.01 *br d*	6.70 *br d*	7.12 *br d*
H-7	7.39 *t*	7.46 *t*	7.46 *t*	7.34 *t*	7.02 *d*	7.13 *d*	7.02 *br d*	7.14 *d*	7.01 *d*	7.21 *d*	7.34 *t*	7.36 *t*	7.37 *t*	7.37 *t*	7.21 *t*	7.40 *t*
H-8	7.21 *br d*	6.81 *br d*	6.80 *br d*	7.16 *br t*	—	—	—	—	—	—	7.14 *br d*	7.12 *br d*	7.18 *br d*	7.19 *br d*	6.79 *br d*	7.23 *br d*
H-9	2.68 *br s*	2.57 *br s*	2.57 *br s*	2.69 *br s*	2.60 *br s*	2.50 *br s*	2.60 *br s*	2.82 *br s*	2.61 *br s*	2.72 *br s*	2.66 *br s*	2.65 *br s*	2.65 *br s*	2.65 *br s*	2.52 *br s*	2.89 *br s*
H-1′	3.15 *dd* 3.08 *dd*	2.76 *dd* 2.48 *br dd*	2.76 *dd* 2.48 *br dd*	3.45 *br d*	3.45 *br d*	3.33 *br d*	3.45 *br d*	3.17 *br d*	3.33 *br d*	3.16 *br d*	1.37 *d*	1.44 *d*	1.54 *d*	1.30 *d*	4.93 *dd* (*t*) 4.98 *dd* (*c*)	1.36 *d*
H-2′	4.95 *dd*	5.23 *br dd*	5.24 *br dd*	5.38 *br t*	5.37 *br t*	5.24 *br t*	5.37 *br t*	5.20 *br t*	5.26 *br t*	5.19 *br t*	3.88 *br q*	4.87 *q*	4.60 *q*	3.25 *q*	5.83 *dd*	3.41 *q*
H-4′	1.60 *m*	2.05 *m*	2.05 *m*	2.10 *m*	2.10 *m*	2.05 *m*	2.10 *m*	2.05 *m*	2.05 *m*	2.05 *m*	5.75 *br t*	1.70 *m* 1.90 *m*	1.69 *m*	1.81 *dt* 1.77 *dt*	1.48 *m*	1.81 *m*
H-5′	2.18 *br dt* 2.10 *br t*										2.91 *dd* 2.85 *dd*	2.05 *m*	2.02 *br dt* 1.93 *br dt*	2.13 *br dt*	1.88 *br dt*	2.12 *br dt*
H-6′	5.14 *br t*	5.02 *br t*	5.04 *br t*	5.08 *br t*	5.08 *br t*	5.07 *br t*	5.08 *br t*	5.07 *br t*	5.07 *br t*	5.09 *br t*	5.16 *tqq*	5.09 *tqq*	5.03 *br t*	5.09 *tqq*	5.05 *tqq*	5.08 *tqq*
H-8′	1.69 *br s*	1.68 *br s*	1.95 *br t*	1.99 *br t*	1.99 *br t*	1.94 *br t*	1.99 *br t*	1.92 *br t*	1.92 *br t*	1.94 *br t*	1.74 *br s*	1.64 *br s*	1.60 *br s*	1.64 *br s*	1.65 *br s*	1.66 *br s*
H-9′	1.64 *br s*	1.56 *br s*	1.56 *br s*	1.61 *br s*	1.60 *br s*	1.57 *br s*	1.60 *br s*	1.56 *br s*	1.56 *br s*	1.57 *br s*	1.68 *br s*	1.55 *br s*	1.49 *br s*	1.57 *br s*	1.55 *br s*	1.59 *br s*
H-10′	1.35 *s*	1.64 *br s*	1.66 *br s*	1.86 *br s*	1.85 *br s*	1.77 *br s*	1.86 *br s*	1.74 *br s*	1.78 *br s*	1.75 *br s*	1.76 *br s*	1.29 *s*	1.45 *s*	1.45 *s*	1.14 *s*	1.45 *s*

*H-11′ 2.10 *m*, H-12′ 5.06 *br t*, H-14′ 1.66 *br s*, H-15′ 1.57 *br s*.

†OAc 2.35 *s*, OH 7.34 *s*.

‡OAc 2.36 *s*, OMe 3.82 *s*.

§OMe 4.07 *s*.

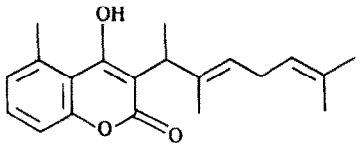
‖OMe 3.80 *s*.

¶OMe 4.07 *s*, OAc 2.36 *s*.

**OH 7.90 *s*.

††H-3′ 3.00 *d*, 2.95 *d*.

J (Hz): 6,7 = 7,8 = 8; 1′,2′ = 4′,5′ = 5′,6′ = 8′,9′ = 7; 6′,8′ = 6′,9′ = 1; (compounds **11** and **12**: 1′,1′ = 14; $1'_1$,2′ = 9; $1'_2$,2′ = 6.5); compound **10**: 1′,1′ = 15; $1'_1$,2′ = 8.5; $1'_2$,2′ = 10; 4′,5′ = 7; 5′,5′ = 15; compound **21**: 4′,5′ = 5′,6′ = 7.5; compound **22**: 1′,2′ = 6.5; compound **23**: 1′,2′ = 6.5; 5′,5′ = 14; compound **24**: 4′,4′ = 14; $4'_1$,5′ = 7; $4'_2$,5 = 8; compound **25**: 3,3′ = 15; 1t′,2′ = 17.5; 1c′,2′ = 11; 1t′,1c′ = 1.



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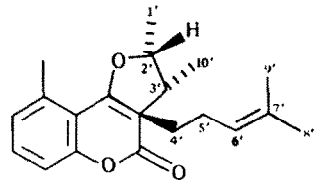
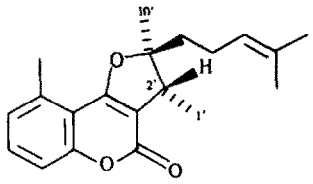


22
23 2'-epi



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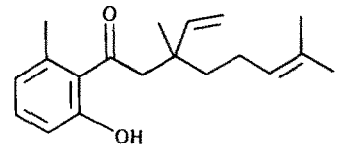

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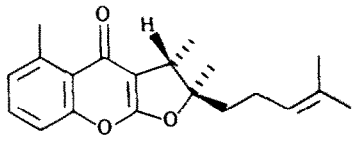

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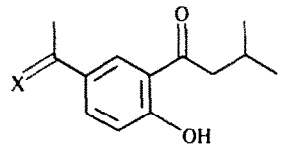
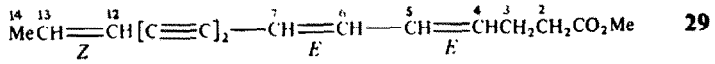
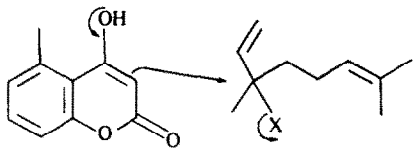


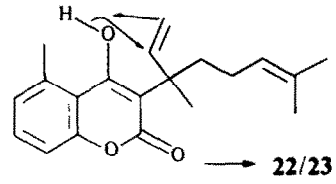
27 X = H,OH
28 X = O



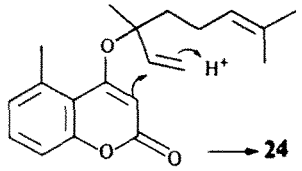
29



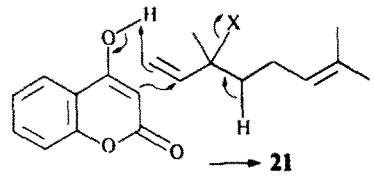
30 31



32



33



30

negative Cotton-effect which may be an indication that the given one may be the absolute configuration if the octant rule can be used.

The structure of **24** also followed from the ^{1}H NMR spectrum (Table 2) which was similar to that of **22**. However, the chemical shifts of some signals were characteristically different. Especially the H-2' quartet was shifted upfield in the spectrum of **24** but also the shifts of H-1' and H-10' were different in the spectra of **22** and **24**. All data therefore agreed with the proposed structure. NOE difference spectroscopy allowed the assignment of the stereochemistry. Thus clear NOEs were observed between H-1' and H-10', between H-10', H-1', H-4' and H-5' as well as between H-9 and H-6. The fragmentation pattern in the mass spectrum of **24** also supported the structure. Especially the presence of *m/z* 228 as base peak was important as this most likely was an indication that after loss of C_6H_{11} (*m/z* 229) further loss of a hydrogen would lead to a stable 3,4-furocoumarin ion.

The molecular formula of **25** indicated that this compound had one carbon less ($C_{19}H_{26}O_2$) and the base peak (*m/z* 135, $C_8H_7O_2$) showed that most likely a simple

derivative of 6-methyl-2-hydroxyacetophenone was present. In agreement with this assumption the ^{1}H NMR spectrum (Table 2) showed the corresponding aromatic signals. Furthermore the signals of a linalyl residue were visible and a pair of doublets at δ3.00 and 2.95. These data only agreed with structure **25**.

The ^{1}H NMR spectrum of **26** (Table 2) was close to that of **24**. However, some signals showed clear differences in the chemical shifts. In particular the H-9 signal was shifted downfield in the spectra of **26**. Accordingly, the presence of chromone was proposed. In agreement with this assumption the IR spectrum displayed a carbonyl band at 1643 cm^{-1}, typical for a cross conjugated keto group. The proposed structure was supported by the mass spectrum where the base peak again was at *m/z* 228. The latter was obviously formed by loss of C_6H_{11} and a hydrogen leading to a 2,3-furocoumarin ion.

Regarding the evolution of the tribe Mutiseae, Cabrera [1] notes various past proposals including origins in tropical America versus the Old Word and relationship to the Heliantheae [21], the Senecioneae [22] or the Cynareae. Most recent authors [23–25] have generally agreed a monophyletic group in what is now usually called the subfamily Cichorioideae near the Cynareae. It is with the latter that the tribe shares common structural features. The Mutisieae shows some structures that might be considered primitive in the subfamily [23] especially in the pollen [26], but the uniformity of some structures in the groups studied by Cabrera [1] allowed him to suggest a recent origin for the group.

Among the commonly recognized subtribes, the least specialized structurally, most widely distributed and probably the oldest would be the Gochnatiinae. The mostly tropical American Mutisiinae and the strictly American Barnadesiinae would be derived from the latter while the highly specialized strictly American Nassauviinae would be a more evolved group.

The chemistry is in part in good agreement with the preceding assumptions. In the Gochnatiinae are several genera (*Actinomeris* [27], *Ainsliaea* [28], *Cnicothamnus* [29], *Dicoma* [30], *Gochnatia* [31], *Moquinia* [32], *Pertya* [33], *Pleiotaxis* [34], *Wunderlichia* [27, 35] which produce typical sesquiterpenes that are also present in the Cynareae. So far only two genera, *Lycoseris* [11] and *Onoseris* [10], gave 5-methylcoumarins which are more widespread in the subtribe Mutisiinae, especially in the basic genus *Gerbera* [1, 3, 6]. In the latter, however, *p*-hydroxyacetophenone derivatives with two prenyl residues are also common [2, 3]. The chemistry of *Mutisia* indicates relationships to the latter by the cooccurrence of 5-methylcoumarins. These compounds are also present in *Brachyclados* which is very close to *Trichocline* with very similar styles [1]. Both the latter genera contain furocoumarins which never have been reported from any Compositae although they are common in the Umbelliferae [36]. So far a eudesmanolide has been reported only from the monotypic genus *Dinoseris* in the Mutisieae [37].

The more evolved subtribe Nassauviinae can be characterized by the occurrence of isocedrene derivatives [38] and perezone and its derivatives [39]. However, from one *Trixis* species several sesquiterpene lactones were reported [38] in part close to those of *Wunderlichia* and *Onoseris*. A few 5-methyl coumarins also are present in representatives of the Nassauviinae (*Jungia* [6] and *Perezia* [9]). Accordingly, the overall picture still is somewhat mixed, but a general trend is relatively clear. Little is known on the chemistry of the Barnadesiinae, we have isolated only simple widespread compounds from *Barnadesia*, *Chuquiraga* and *Dasyphyllum* species. The cooccurrence of several characteristic types of natural products in different subtribes is a possible indication of close relationships between the elements tested and might support the proposal that they are recently evolved [1].

EXPERIMENTAL

The air dried plant material was collected in February 1985 in Argentina and extracted with Et_2O–MeOH–petrol (1:1:1). The extracts obtained were first separated by CC (silica gel) and further by TLC (silica gel, PF 254) as reported previously [39]. Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material and by co-TLC. The extract of the aerial parts of *Mutisia spinosa* (600 g, voucher RMK 9397, all deposited in the US National Herbarium, Washington) gave CC fractions as follows: 1 (petrol), 2 (Et_2O–petrol, 1:10), 3 (Et_2O–petrol, 1:3), 4 (Et_2O–petrol, 1:1 and 3:1) and 5 (Et_2O and Et_2O–MeOH, 10:1). TLC (petrol) of fraction 1 gave 11 mg β-selinene, 1 mg tridecapantaynene and 3 mg trideca-1,11-dien-3,5,7,9-tetrayne. Fraction 2 gave 300 mg nearly pure geranyl acetate and fraction 3 was separated again by medium pressure chromatography (MPC) (silica gel, 30–60 μm, Et_2O–petrol, 1:9–1:3). Fractions 1–5 gave by TLC (Et_2O–petrol, 1:9) 10 mg geranyl acetate, 10 mg caryophyllen-1,10-epoxide, 2 mg phytol and 10 mg α-bisabol. Fractions 6–9 gave 150 mg α-bisabolol and fractions 13–15 (Et_2O–petrol, 1:3) two mixtures (R_f 0.50 and R_f 0.45). The latter gave by repeated TLC (Et_2O–$CHCl_3$–C_6H_6, 1:5:5) 3 mg **3** (R_f 0.65) and the former (same solvents) afforded 5 mg **12** (R_f 0.58) and 10 mg **11** (R_f 0.53). HPLC (RP 8, MeOH–H_2O, 9:1, *ca* 100 bar, flow rate 3 ml/min) of MPC 16–18 gave 2 mg **11** (R_t 3.3 min) and 2 mg **12** (R_t 8.3 min). TLC of MPC 19–20 (Et_2O–petrol, 1:3) gave 5 mg **13** (R_f 0.4) and a mixture which by HPLC (RP8, MeOH–H_2O, 3:1) afforded 10 mg **2** (R_t 2.4 min) and two mixtures (R_t 2.2 min and R_t 2.7 min). TLC (Et_2O–C_6H_6–$CHCl_3$, 1:5:5) of the former gave 20 mg **6** (R_f 0.67) and 10 mg **8** (R_f 0.50). TLC of the third HPLC fraction (same solvent) afforded 5 mg **4** (R_f 0.63). TLC of MPC 23–25 (Et_2O–petrol, 1:3) gave 90 mg **9** (R_f 0.35) and TLC of MPC 26–29 afforded by HPLC (RP8, MeOH–H_2O, 3:1) gave 10 mg **9** (R_t 2.0 min). TLC of MPC 30–35 (Et_2O–petrol, 1:1) afforded 2 mg **1** (R_f 0.70), 1 mg **5** (R_f 0.72) and 5 mg **10** (R_f 0.55). TLC of MPC 36–40 (Et_2O–petrol, 1:1) gave 1 mg 6-methylsalicylic acid (R_f 0.45). CC fractions 4 and 5 gave nothing of interest. The extract of 130 g roots gave by CC (silica gel) 5 mg tridecapentaynene, 5 mg trideca-1,11-dien-3,5,7,9-tetrayne, 10 mg phytol and two polar fractions: 3 (Et_2O–petrol, 3:1) and 4 (Et_2O). TLC of fraction 3 (Et_2O–petrol, 1:1) gave 200 mg **14** (R_f 0.75) and 300 mg **13** (R_f 0.55). Fraction 4 gave 1.5 g crude **17**, which was only purified in part by TLC (50 mg, Et_2O–petrol, 3:1) and also transformed to **15**, **16** and **18–20** (see below).

The extract of the aerial parts of *M. retrorsa* Cav. (200 g, voucher RMK 9369) gave by CC and TLC (silica gel) 1 mg germacrene D, 30 mg lupeyl acetate and 20 mg **29** (TLC, Et_2O–petrol, 1:3, R_f 0.62), colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2200, 2130 (C≡C), 1745 (CO_2R), 1640, 1625, 990 [$(CH{=}CH)_2$]; UV $\lambda_{max}^{Et_2O}$: 336, 312, 296 nm; MS *m/z* (rel. int.): 228.115 $[M]^+$ (49) (calc. for $C_{15}H_{16}O_2$: 228.115), 169 $[M-CO_2Me]^+$ (54), 155 $[M-CH_2CO_2Me]^+$ (68), 153 $[155-H_2]^+$ (100), 141 (53), 129 (52), 115 (56); ^{1}H NMR (C_6D_6): 2.02 (*t*, H-2), 2.12 (*br dt*, H-3), 5.35 (*dt*, H-4), 5.70 (*dd*, H-5), 6.48 (*dd*, H-6), 5.38 (*br d*, H-7), 5.40 (*br d*, H-12), 5.68 (*dq*, H-13), 1.69 (*dd*, H-14), 3.33 (s, OMe)

[J (Hz): 2,3 = 3,4 = 13,14 = 7; 4,5 = 6,7 = 15; 5,6 = 12,13 = 10; 12,14 = 1.5].

The extract of the aerial parts of *T. sinuata* (Don.) Cabrera (250 g, voucher RMK 9432) and of the roots (100 g) (isolated amounts in parentheses) gave by CC and TLC (see above) 10 mg (−)-caryophyllen-1,10-epoxide, 50 mg (−) lupeyl acetate, 10 mg (10 mg) 6-acetyl-5-hydroxy-2-isopropenyl-2,3-dihydrobenzo furane, 50 mg (30 mg) isoimperatorin, 300 mg (−)-trichoclin, 50 mg (40 mg) xanthotoxin, 100 mg (40 mg) bergapten, 400 mg (20 mg) isopimpinellin, 30 mg (10 mg) phellopterin, 50 mg imperatorin, 30 mg 7-isopentenyloxy coumarin and only the roots 20 mg psoralen.

The extract of the aerial parts of *B. megalanthus* Spegazzini (200 g, voucher RMK 9390) gave by CC and TLC (see above) 30 mg 7-isopentenyloxy coumarin, 10 mg bergapten, 50 mg imperatorin, 15 mg isoimperatorin, 200 mg oxypeucedanin and 50 mg **27**. The extract from the roots (200 g) gave on standing at −20° in Et_2O 150 mg bergaptene. CC (silica gel) of the mother liquor afforded three fractions (1: Et_2O–petrol, 1:1, 2: Et_2O and 3: Et_2O–MeOH, 9:1) which were further separated by TLC (silica gel, PF 254). Fraction 2 gave 100 mg psoralene and 20 mg **27** while fraction 3 gave 50 mg bergaptene. TLC (Et_2O–petrol, 1:3) of fraction 1 gave three bands (1/1–1/3). TLC of 1/1 (Et_2O–petrol, 1:9, two developments) gave 10 mg **22** (R_f 0.23). HPLC of 1/2 (RP 18, MeOH–H_2O, 9:1, *ca* 100 bar, flow rate 3 ml/min) gave 10 mg 6-acetyl-2,2-dimethyl chromene (R_t 2.0 min), 10 mg **28** (R_t 2.6 min), 10 mg **25** (R_t 4.2 min), 5 mg **21** and **23** (*ca* 4:5) (R_t 6.5 min), 5 mg **22** (R_t 7.0 min), 5 mg **24** (R_t 7.5 min) and 2 mg **26** (R_t 8.5 min). Fraction 1/3 contained 5 mg **27**. The mixture of **21** and **23** could be separated by TLC (Et_2O–petrol, 1:9, **21**: R_f 0.70, **23**: R_f 0.72, after 10 developments).

6-Hydroxy-7(9)-dehydro-6,7-dihydrogeranyl acetate (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (OAc); MS *m/z* (rel. int.): 152.110 $[M-HOAc]^+$ (8) (calc. for $C_{10}H_{16}O$: 152.110), 135 $[152-OH]^+$ (28), 71 $[C_4H_7O]^+$ (100).

6-Peroxy-7(9)-dehydro-6,7-dihydrogeranyl acetate (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OOH), 1740, 1245 (OAc), 3050, 1650, 915 (C=CH_2); MS *m/z* (rel. int.): 195.139 $[M-OOH]^+$ (0.5) (calc. for $C_{12}H_{19}O_2$: 195.139), 169 $[M-OAc]^+$ (1), 151 $[169-H_2O]^+$ (4), 135 $[195-HOAc]^+$ (14), 107 (48), 93 (59), 81 (89), 69 (100), 68 (86), 55 (94). Reaction of **2** (5 mg, $CDCl_3$) with triphenyl phosphine afforded **1**, identical with the natural compound (^1H NMR, TLC); 3 mg **2** on heating with 0.5 ml Ac_2O (1 hr, 70°) gave 2 mg **3**, identical with the natural product (^1H NMR, TLC).

6-Oxo-7(9)-dehydro-6,7-dihydrogeranyl acetate (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1235 (OAc), 1680, 1630 (C=CC=O); MS *m/z* (rel. int.): 151.112 $[M-OAc]^+$ (8) (calc. for $C_{10}H_{15}O$: 151.112), 69 $[C_3H_5CO]^+$ (100).

6-Peroxy-7(9)-dehydro-2,3,6,7-tetrahydrogeranyl acetate (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OOH), 1740, 1240 (OAc); MS *m/z* (rel. int.): 197.154 $[M-OOH]^+$ (1) (calc. for $C_{12}H_{21}O_2$: 197.154), 137 $[197-AcOH]^+$ (28), 81 $[C_6H_9]^+$ (100); $[\alpha]_D$ = −6 ($CHCl_3$; *c* 0.54).

6-Hydroxy-7(9)-dehydro-6,7-dihydroneryl acetate (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740, 1240 (OAc); MS *m/z* (rel. int.): 152.120 $[M-HOAc]^+$ (7) (calc. for $C_{10}H_{16}O$: 152.120), 135 $[152-OH]^+$ (25), 71 $[C_4H_7O]^+$ (100).

6-Peroxy-7(9)-dehydro-6,7-dihydroneryl acetate (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OOH), 1745, 1250 (OAc); EIMS *m/z* (rel. int.): 195.139 $[M-OOH]^+$ (0.7) (calc. for $C_{12}H_{19}O_2$: 195.139), 169 $[M-OAc]^+$ (12), 135 $[195-HOAc]^+$ (19), 55 (100); CIMS: 211 $[M+1-H_2O]^+$ (2.5), 195 $[M+1-H_2O_2]^+$ (5.3), 151 $[211-HOAc]^+$ (100). Compound **6** (10 mg) was heated in 0.5 ml Ac_2O for 1 hr at 70°. TLC (silica gel, Et_2O–petrol, 1:3) gave 5 mg **7**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1250 (OAc), 1685, 1630 (C=C–C=O); MS *m/z* (rel. int.): 210.126 $[M]^+$ (0.2) (calc. for $C_{12}H_{18}O_3$: 210.126), 168 $[M-ketene]^+$ (1.5), 150 $[M-HOAc]^+$ (9), 69 $[C_3H_5CO]^+$ (100).

7-Peroxy-5,6E-dehydro-6,7-dihydroneryl acetate (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OOH), 1740, 1245 (OAc); MS *m/z* (rel. int.): 195.138 $[M-OOH]^+$ (1.3) (calc. for $C_{12}H_{19}O_2$: 195.138), 135 $[195-HOAc]^+$ (36), 71 $[C_4H_7O]^+$ (100); CIMS *m/z* 195 $[M+1-H_2O_2]^+$ (5), 135 $[195-HOAc]^+$ (100).

7-Peroxy-5,6E-dehydro-6,7-dihydrogeranyl acetate (**9**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3570 (OOH), 1740, 1245 (OAc); MS *m/z* (rel. int.): 195.138 $[M-OOH]^+$ (5) (calc. for $C_{12}H_{19}O_2$: 195.138), 135 $[195-HOAc]^+$ (100); CIMS *m/z* 229 $[M+1]^+$ (1), 211 $[229-H_2O]^+$ (3), 195 $[229-H_2O_2]^+$ (2.5), 135 $[195-HOAc]^+$ (100).

Mutisicoumarin (**10**). Colourless crystals, mp 59°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1735, 1635, 1605 (coumarin); MS *m/z* (rel. int.): 328.167 $[M]^+$ (24) (calc. for $C_{20}H_{24}O_4$: 328.167), 313 $[M-Me]^+$ (3), 310 $[M-H_2O]^+$ (3), 243 $[313-C_5H_{10}]^+$ (24), 201 $[M-HOC(Me)CH_2CH_2CH{=}CMe_2]^+$ (74), 69 $[C_5H_9]^+$ (100).

5-Methyl-3-geranyl-3-hydroxycoumarane (**11**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1730, 1605 (PhCO); MS *m/z* (rel. int.): 300.173 $[M]^+$ (1) (calc. for $C_{19}H_{24}O_3$: 300.173), 282 $[M-H_2O]^+$ (1.5), 228 $[282-C_4H_6]^+$ (34), 164 $[M-C_{10}H_{16}$, McLafferty$]^+$ (48), 69 $[C_5H_9]^+$ (100).

5-Methyl-3-farnesyl-3-hydroxy-coumarane (**12**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1730, 1605 (PhCO); MS *m/z* (rel. int.): 368.235 $[M]^+$ (2) (calc. for $C_{24}H_{32}O_3$: 368.235), 350 $[M-H_2O]^+$ (0.6), 218 $[M-C_{11}H_{18}]^+$ (3), 164 $[M-$farnesene, McLafferty$]^+$ (36), 163 $[M-$farnesyl$]^+$ (23), 136 $[164-CO]^+$ (26), 135 $[163-CO]^+$ (32), 69 $[C_5H_9]^+$ (100); ^{13}C NMR ($CDCl_3$): (C-3–C-9) δ103.1 *s*, 199.1 *s*, 117.4 *s*, 143.8 *s*, 123.4 *d*, 138.2 *d*, 110.2 *d*, 170.7 *s*; (C-1′–C-15′) 34.6 *t*, 144.4 *d*, 140.5 *s*, 39.9 *t*, 26.3 *t*, 123.6 *d*, 135.7 *s*, 39.6 *t*, 26.7 *t*, 124.3 *d*, 131.3 *s*, 25.7 *q*, 16.0 *q*, 16.4 *q*, 17.7 *q*.

5-Methyl-4-hydroxy-3-farnesylcoumarin (**14**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3350 (OH), 1720, 1625, 1605 (coumarin); MS *m/z* (rel. int.): 380.235 $[M]^+$ (9) (calc. for $C_{25}H_{32}O_3$: 380.235), 311 $[M-C_5H_9]^+$ (9), 243 $[M-C_{10}H_{17}]^+$ (26), 189 (44), 135 (54), 109 (56), 69 $[C_5H_9]^+$ (100).

5-Methyl-2,8-dihydroxy-3-farnesylchromone (**17**). Yellow, unstable oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610, 3320 (OH), 1670, 1615, 1570 (PhCO); MS *m/z* (rel. int.): 396.230 $[M]^+$ (9) (calc. for $C_{25}H_{32}O_4$: 396.230), 327 $[M-C_5H_9]^+$ (7), 259 $[M-C_{10}H_{17}]^+$ (22), 151 $[C_8H_7O_3]^+$ (96), 123 $[151-CO]^+$ (28), 69 $[C_5H_9]^+$ (100). Compound **17** (30 mg) in 0.5 ml Ac_2O were heated for 1 hr at 70°. TLC (Et_2O–petrol, 1:1) afforded 20 mg **15**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3520 (OH), 1765 (PhOAc), 1720, 1625, 1600 (coumarin); MS *m/z* (rel. int.): 438.230 $[M]^+$ (8) (calc. for $C_{27}H_{34}O_5$: 438.230), 396 $[M-$ketene$]^+$ (3), 369 $[M-C_5H_9]^+$ (2.5), 301 $[M-C_{10}H_{17}]^+$ (11), 259 $[301-$ketene$]^+$ (29), 69 $[C_5H_9]^+$ (100). To 20 mg **15** excess of CH_2N_2 in Et_2O was added. TLC (Et_2O–petrol, 1:1) gave 4 mg **16** (R_f 0.67) and 12 mg **20** (R_f 0.60). Compound **16**: Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (OAc), 1730, 1635, 1620 (coumarin); MS *m/z* (rel. int.): 452.256 $[M]^+$ (21) (calc. for $C_{28}H_{36}O_5$: 452.256), 383 $[M-C_5H_9]^+$ (38), 315 $[M-C_{10}H_{17}]^+$ (100), 69 $[C_5H_9]^+$ (88); compound **20**: Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (PhOAc), 1635, 1580 (PhCO); MS *m/z* (rel. int.): 452.256 $[M]^+$ (52) (calc. for $C_{28}H_{36}O_5$: 452.256), 383 $[M-C_5H_9]^+$ (100), 315 $[M-C_{10}H_{17}]^+$ (37), 261 $[M-C_{14}H_{23}]^+$ (66). To 20 mg **17** excess of CH_2N_2 in Et_2O was added. TLC (Et_2O–petrol, 1:1) gave 3 mg **19** (R_f 0.52) and 12 mg **18** (R_f 0.47). Compound **18**: Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1680, 1570 (PhCO); MS *m/z* (rel. int.): 410.246 $[M]^+$ (2) (calc. for $C_{26}H_{34}O_4$: 410.246), 341 $[M$

$-C_5H_9]^+$ (76), 273 $[M-C_{10}H_{17}]^+$ (11), 219 $[M-C_{14}H_{23}]^+$ (100); compound **19**: Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1685, 1610, 1570 (PhCO); MS *m/z* (rel. int.): 410.246 $[M]^+$ (1.5) (calc. for $C_{26}H_{34}O_4$: 410.246), 341 $[M-C_5H_9]^+$ (4), 273 $[M-C_{10}H_{17}]^+$ (20), 243 $[273-CH_2O]^+$ (40), 69 $[C_5H_9]^+$ (100).

Brachycoumarin (**21**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1730, 1635 (coumarin); MS *m/z* (rel. int.): 312.173 $[M]^+$ (16) (calc. for $C_{20}H_{24}O_3$: 312.173), 243 $[M-C_5H_9]^+$ (14), 230 $[M-C_6H_{10}]^+$ (86), 229 $[M-C_6H_{11}]^+$ (100), 215 $[230-Me]^+$ (47), 203 $[M-C_8H_{13}]^+$ (66), 136 $[C_8H_8O_2]^+$ (70), 135 $[C_8H_7O_2]^+$ (54), 121 $[136-Me]^+$ (68), 69 $[C_5H_9]^+$ (34).

Cycloisobrachycoumarin (**22**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725, 1630, 1605 (coumarin); MS *m/z* (rel. int.): 312.173 $[M]^+$ (15) (calc. for $C_{20}H_{24}O_3$: 312.173), 230 $[M-C_6H_{10}$, McLafferty$]^+$ (100), 229 $[M-C_6H_{11}]^+$ (84), 215 $[230-Me]^+$ (61), 187 $[230-MeCO]^+$ (22), 135 $[C_8H_7O_2]^+$ (56); $[\alpha]_D^{24°} = -52$ ($CHCl_3$; *c* 0.97); CD (MeCN): $\Delta\varepsilon_{318} = -2.15$, $\Delta\varepsilon_{282} = -4.3$.

2'-Epicycloisobrachycoumarin (**23**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1635 (coumarin); MS *m/z* (rel. int.): 312.173 $[M]^+$ (19) (calc. for $C_{20}H_{24}O_3$: 312.173), 230 $[M-C_6H_{10}$, McLafferty$]^+$ (100), 229 $[M-C_6H_{11}]^+$ (80), 215 $[230-Me]^+$ (72), 135 $[C_8H_7O_2]^+$ (39).

Cyclobrachycoumarin (**24**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1635, 1605 (coumarin); MS *m/z* (rel. int.): 312.173 $[M]^+$ (14) (calc. for $C_{20}H_{24}O_3$: 312.173), 230 $[M-C_6H_{10}]^+$ (26), 229 $[M-C_6H_{11}]^+$ (46), 228 $[229-H]^+$ (100), 215 $[230-Me]^+$ (16), 187 $[215-CO]^+$ (61), 135 $[C_8H_7O_2]^+$ (26); $[\alpha]_D^{24°} = -6$ ($CHCl_3$; *c* 0.45).

Norbrachycoumarin (**25**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600–2600, 1640, 1610, 1580 (hydrogen bonded PhCO); MS *m/z* (rel. int.): 286.193 $[M]^+$ (5) (calc. for $C_{19}H_{26}O_2$: 286.193), 271 $[M-Me]^+$ (12), 203 $[M-C_6H_{11}]^+$ (7), 135 $[C_8H_7O_2]^+$ (100); $[\alpha]_D^{24°} = -8$ ($CHCl_3$; *c* 0.77).

Brachychromone (**26**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1643 (chromone); MS *m/z* (rel. int.): 312.173 $[M]^+$ (28) (calc. for $C_{20}H_{24}O_3$: 312.173), 229 $[M-C_6H_{11}]^+$ (73), 228 $[229-H]^+$ (100), 135 $[C_8H_7O_2]^+$ (63), 69 $[C_5H_9]^+$ (58).

2-Isovaleroyl-4-[1-hydroxyethyl]-phenol (**27**). Colourless crystals, mp 150°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 3500–2600, 1645, 1615 (hydrogen bonded PhCO); MS *m/z* (rel. int.): 222.126 $[M]^+$ (32) (calc. for $C_{13}H_{18}O_3$: 222.126), 207 $[M-Me]^+$ (62), 189 $[207-H_2O]^+$ (10), 165 $[M-C_4H_9]^+$ (100), 147 $[165-H_2O]^+$ (31), 119 $[147-CO]^+$ (11); $[\alpha]_D^{24°} = -4$ ($CHCl_3$; *c* 2.5); ^1H NMR ($CDCl_3$): δ 7.75 (*d*, H-3), 7.44 (*dd*, H-5), 6.93 (*d*, H-6), 4.87 (*q*, H-7), 1.48 (*d*, H-8); iVal: 2.85 *d*, 2.28 *tqq*, 1.00 *d* (6H). [*J* (Hz): 3, 5 = 2; 5, 6 = 8; 2', 3' = 3', 4' = 3', 5' = 7]. Compound **27** (10 mg) was stirred for 2 hr in Et_2O with 50 mg MnO_2. TLC (Et_2O–petrol, 1:1) gave 5 mg **28**, identical with authentic material (^1H NMR, co-TLC).

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