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Three further 1,9-diarylnonanoid 3-*O*-glycosides from *Erica cinerea* ☆

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(−)-(3*S*,7*S*)-3″-Hydroxyericanone 3-*O*-β-D-glucopyranoside
(−)-(3*S*)-3″-Hydroxy-α-ericadione 3-*O*-β-D-glucopyranoside

ABSTRACT

In addition to the six diarylnonanoids and diarylnonanoid 3-*O*-glucosides previously reported from *Erica cinerea*, the multistep chromatographic processing of the acetone extract of the fresh aerial parts resulted in the isolation of three more representatives as glycosides derived from either (−)-ericanone or (−)-α-ericadione. From the spectroscopic data, the new structures were elucidated as (−)-(3*S*,7*S*)-ericanone 3-*O*-β-D-xylopyranoside, (−)-(3*S*,7*S*)-3″-hydroxyericanone 3-*O*-β-D-glucopyranoside, and (−)-(3*S*)-3″-hydroxy-α-ericadione 3-*O*-β-D-glucopyranoside respectively. In the ^{1}H and ^{13}C NMR spectra run in CD_3OD, the latter metabolite was as (−)-α-ericadione 3-*O*-β-D-glucopyranoside, also found as a permanent mixture of the major *s-trans* (70%) and the minor *s-cis* (30%) conformers. Such result —in connection with the protic solvent— seems to have never been reported earlier for α-alkadiones. Moreover, mild acid hydrolysis of such a glucoside led directly to the 3,4-dehydrated aglycone moiety accompanied by its 6,7-dehydrated tautomer, according to two successive dehydrations of the anticipated aglycone. Furthermore, although missing in this species, the postulated β-ericadione continues to be regarded as an essential intermediate at the crossroads of the biogenesis of most of the *E. cinerea* 1,9-diarylnonanoids.

The previous phytochemical investigation of *Erica cinerea* L. fresh aerial parts' acetone extract afforded the linear 1,9-diarylnonanoid (3*S*,7*S*)-ericanone (**1**), the partly cyclized (3*S*)-3,7-anhydro-6,7-dehydroericanone (**5**), their corresponding 3-*O*-β-D-glucosides **2** and **6** as well as (3*S*,6*E*)-6,7-anhydroericanone 3-*O*-β-D-glucoside (**7**) and (3*S*)-α-ericadione 3-*O*-β-D-glucoside (**8**).[1,2] Continuation of the multistep chromatographic process of the ethyl acetate soluble part, yielded three extra linear 1,9-diarylnonanoid 3-*O*-glycosides **3**, **4**, and **9**, unknown in the plant kingdom.[3] On the basis of spectroscopic evidence (UV, MS, and NMR), the newly reported compounds were determined to be derived from either (3*S*,7*S*)-ericanone or (3*S*)-α-ericadione. With the unusual α-alkadione type structure for a natural product, metabolite **9** was like **8**, split into the major *s-trans* (70%) and the minor *s-cis* (30%) conformers in NMR protic solvent. Such a behavior which is also shared by commercially 2,3-pentanedione, seems to have never been described for α-diketones. Finally, given the striking relationship between all these 1,9-diarylnonanoids, they are therefore biogenetically regarded as deriving from a mutual 3-hydroxy-5,7-diketo type precursor, namely β-ericadione.

To compound **3**, obtained as a white amorphous powder, $[\alpha]_D^{22}$ −18.2 (c 0.018, MeOH), was assigned the molecular formula $C_{26}H_{34}O_9$ by HRESMS (found: 513.2095; calcd: 513.2100 for $[M+Na]^+$). As predicted by the coincident UV spectra (λ_{max}^{MeOH} nm: 280) and the very close chromatographic mobilities (TLC and HPLC), the ^{1}H and ^{13}C NMR data (Table 1) showed a close relationship with ericanone 3-glucoside (**2**).[1] The difference of 30 amu (CH_2O) between them, was reflected in the ^{1}H and ^{13}C NMR features relative to the sugar region revealing one oxycarbon less for **3**. Thus, the glucosyl unit in **2** was replaced by a pentosyl in **3**. Mild acid hydrolysis of the latter metabolite gave (−)-ericanone (**1**) and xylose which was determined by GC analysis of the TMSi derivative. The identical ^{1}H and ^{13}C NMR data of the ericanone part in **2** and **3**, and particularly the downfield shifts of one oxymethine (H-3: δ 4.16, br quint, J = 6.3 Hz; C-3: δ 76.8) supported including this position in an ether linkage with the β-D-xylosyl unit (H-1‴: δ 4.28, d, J = 7.8 Hz). In the HMBC spectrum virtually similar to that of **2**, the ^{3}J cross-peaks displayed by H-3 with the anomeric C-1‴ (δ 104.1) and in turn by C-3 with the anomeric proton confirmed this attachment. On the basis of spectral evidence for a β-D-xylopyranoside,[4–9] compound **3** was identified as the newly reported ericanone 3-*O*-β-D-xylopyranoside. Laevorotatory as **1** and **2**, this metabolite must also have the (3*S*,7*S*)-configuration.

Contrary to ericanone 3-*O*-β-D-xyloside (**3**), compound **4**, the most polar in this series differed from the reference compound **2** only by the aglycone moiety and particularly by the outer aromatic ring(s) as indicated by the UV spectrum: λ_{max}^{MeOH} 284 nm. With the

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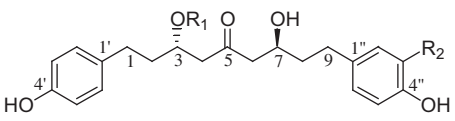
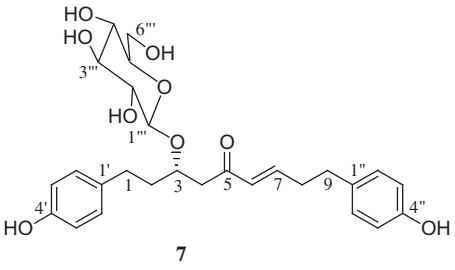


1 $R_1 = R_2 = H$
2 $R_1 = \beta$-D-Glc; $R_2 = H$
3 $R_1 = \beta$-D-Xyl; $R_2 = H$
4 $R_1 = \beta$-D-Glc; $R_2 = OH$



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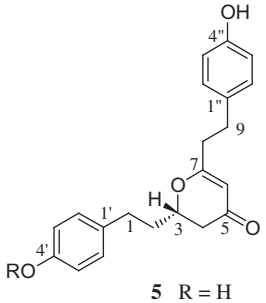
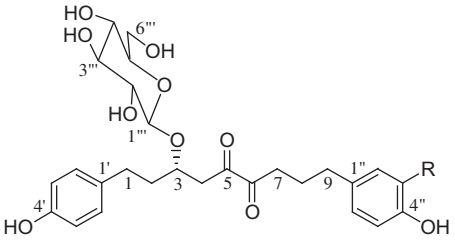


5 R = H
6 R = β-D-Glc



8 R = H
9 R = OH

molecular formula $C_{27}H_{36}O_{11}$ given by HRESMS (found: 559.2171; calcd: 559.2211 for $[M+Na]^+$) and $[\alpha]_D^{19}$ −14.5 (c 0.012, MeOH), compound **4** showed only one oxygen atom more when compared to **2**. This heteroatom was located on an aromatic ring, since a *p*-hydroxyphenyl unit in **2** was replaced by a catechyl ring, as indicated by the ^1H and ^{13}C NMR data (Table 1). Indeed, in agreement with the apparent UV bathochromic shift of 4 nm with respect to both metabolites **2** and **3**, the resulting 1,3,4-trisubstituted aromatic ring was fully characterized by the particular *ortho*-dioxy system with two *O*-bonded quaternary C at δ 146.1 (C-3″) and δ 144.2 (C-4″). According to the HMBC spectrum, the catechyl part was linked to C-9 as supported by the ^3J cross peaks recorded between H_2-9 (δ 2.64 and 2.48) and both C-2″ (δ 116.3) and C-6″ (δ 120.7), and between H-8 (δ 1.67) and C-1″ (δ 134.4). The remaining *p*-hydroxyphenyl was still attached to C-1 as shown by the main ^3J connectivities displayed by C-1′ (δ 135.0) with H-2a (δ 1.87) and H-2b (δ 1.77). Ultimately, the 3-*O*-glucosyl linkage was evidenced as mentioned above for **3**. From these results, the novel (3*S*,7*S*)-3″-hydroxyericanone 3-*O*-β-D-glucopyranoside structure was attributed to laevorotatory **4**.

In comparison with **8**,[2] glycoside **9** was also isolated as a viscous mass from a methanol solution. With a lower mobility on silica gel TLC, it exhibited a similar UV spectrum as well as quasi-coincident ^1H and ^{13}C NMR spectra in CD_3OD (Table 1). Except for the variant aromatic region, all other NMR signals were superimposable. They really supported mixed conformers as for **8**, split into the major *s-trans* (70%) and the minor *s-cis* (30%). Owing to the molecular formula $C_{27}H_{34}O_{11}$ established by HRESMS (found: 557.2151; calcd: 557.2211 for $[M+Na]^+$) indicating 16 amu more, glucoside **9** was consequently considered as the oxy derivative of **8**. Once again, the only difference was the replacement of one *p*-hydroxyphenyl unit in **8** by a catechyl ring attached to C-9 as reported above for **4**. Hence, the new 1-(*p*-hydroxyphenyl)-9-(3,4-dihydroxyphenyl)-3-hydroxynonan-5,6-dione 3-*O*-β-D-glucopyranoside structure was assigned to **9**. Named 3″-hydroxy-α-ericadione 3-*O*-β-D-glucoside, this metabolite was like **8** with the (3*S*)-configuration according to $[\alpha]_D^{22}$ −10.7 (c 0.075, MeOH). The mixed conformers for such a product were obviously characterized by the three distinct NMR signal pairs of diagnostic value for H-3, C-5, and C-6, respectively.[2] With respect to the α-dione minor *s-cis* conformer signals (H-3: δ 4.16, br quint, J = 6.5 Hz; C-5: δ 206.1; C-6: δ 206.9),[10] those of the major *s-trans* conformer were, as previously reported for **8**, shifted upfield: a scarcely discernible move for H-3 (δ 4.10, br quint, J = 6.5 Hz; $\Delta\delta$ −0.06) contrasting with a more pronounced shift ($\Delta\delta$ −12.7) for both C-5 (δ 193.4) and C-6 (δ 194.2). Without neglecting H-bond consequences, the chemical shift variation of the carbonyls was so high because these groups were directly affected by the torsion angle around the inter-carbonyl bond, in terms of steric hindrance and anisotropy. To conclude, such a permanent conformational equilibrium in CD_3OD —excluding a possible mixture of other different diones (β-, γ- and/or δ-)— was of course supported by joint C-atoms —C-α,α′ and C-β,β′— close to the 5,6-dione bifunction for both conformers, namely C-3 (δ 76.8), C-4 (δ 44.8), C-7 (δ 41.1), and C-8 (δ 46.4).[2]

As previously reported, the α-ericadione bifunction is unusual in the natural open-chain polyketides —1,7-diarylheptanoids and 1,9-diarylnonanoids— and most likely in long-chain natural products in general in that it has an α-alkadione structural feature.[2] In CD_3OD, H-bonds between the protic solvent and each carbonyl group must play a key role on the ongoing balance between the major *s-trans* and the minor *s-cis* rotamers. The stability of the latter species is probably enhanced by the reduced repulsive effect between the carbonyl oxygen atoms. However, no reference in the literature relative to the NMR of simple α-alkadiones, suggests mixed conformers for such products because the spectra are usually run in $CDCl_3$.[9,11–15] In order to confirm clearly the above mentioned protic solvent effect, the ^{13}C NMR of available 2,3-pentanedione was undertaken in $CDCl_3$ and CD_3OD respectively.[16] Contrary to the expected five signals in the aprotic solvent, among which the carbonyls belonging to the unique *s-trans* species (C-2: δ 197.5; C-3: δ 199.8), five more signals were exhibited in the protic solvent. They suggested unambiguously mixed conformers in the permanent ratio 70:30. Each one was characterized by a signal pair: δ 198.7 (C-2) and δ 200.9 (C-3) for the major *s-trans* and δ 209.8 (C-2; $\Delta\delta$ +11.1) and δ 211.8 (C-3; $\Delta\delta$ +10.9) for the minor *s-cis*. This equilibrium was maintained without any change even

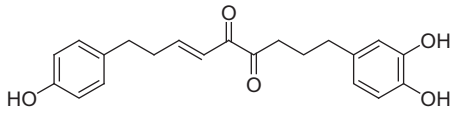
Table 1
^{13}C NMR (125 MHz) and ^{1}H NMR (500 MHz) data for ericanone 3-xyloside (**3**), 3″-hydroxyericanone 3-glucoside (**4**) and major *s-trans*-3″-hydroxy-α-ericadione 3-glucoside (**9**) in CD_3OD (δ ppm; *J* Hz)

C/H	3			4			9		
	^{13}C	^{1}H	HMBC	^{13}C	^{1}H	HMBC	^{13}C	^{1}H	HMBC
1	31.4	2.59 m	C-3; C-2′,6′	31.4	2.58 m	C-3; C-2′,6′	31.4	2.64 m	C-3; C-2′,6′
2	38.6	1.80 br hext (7.0)	C-4; C-1′	38.5	1.87 br hext (7.5)	C-4; C-1′	38.4	1.87 m	C-4; C-1′
		1.72 m	C-4; C-1′		1.77 m	C-4; C-1′		1.79 m	C-4; C-1′
3	76.8	4.16 br quint (6.3)	C-1; C-5; C-1‴	76.4	4.20 br quint (6.4)	C-1; C-5; C-1‴	76.8	4.10 br quint (6.5)	C-1; C-5; C-1‴
4	49.5	2.81 dd (16.7; 7.3)		49.2	2.84 dd (16.8; 7.2)		44.8	2.62 m	
		2.56 m			2.56 m			2.50 dd (16.1; 6.4)	
5	211.0			211.2			193.4		
6	52.0	2.60 m		51.9	2.58 m		194.2		
7	68.1	4.00 br quint (6.2)	C-5; C-9	68.1	4.03 br quint (6.3)	C-5; C-9	41.1	2.53 t (8.1)	C-5
8	40.5	1.65 dt (8.0; 6.1)	C-1″	40.4	1.67 dt (8.0; 6.3)	C-1″	46.4	2.77 m	C-6; C-1″
9	31.9	2.62 m	C-7; C-2″,6″	32.1	2.64 m	C-7; C-2″; C-6″	32.1	2.73 t (7.3)	C-6; C-2″; C-6″
		2.53 m	C-7; C-2″,6″			2.48 m	C-7; C-2″; C-6″		
1′	134.4[a]			135.0			134.7		
2′,6′	130.4[b]	6.97 d (8.4)	C-1; C-4′	130.4	7.02 d (8.5)	C-1; C-4′	130.7	7.02 d (8.5)	C-1; C-4′
3′,5′	116.1	6.65 d (8.4)	C-1′	116.1	6.67 d (8.5)	C-1′	116.1[a]	6.68 d (8.5)	C-1′
4′	156.4[c]			156.3			156.3		
1″	134.2[a]			134.4			133.7		
2″	130.3[b]	6.97 d (8.4)	C-9; C-4″	116.3	6.63 d (2.0)	C-9; C-4″; C-6″	116.4	6.63 d (2.0)	C-9; C-4″
3″	116.1	6.64 d (8.4)	C-1″	146.1		C-1″	146.2		
4″	156.3[c]			144.2			144.6		
5″	116.1	6.64 d (8.4)	C-1″	116.6	6.66 d (8.0)	C-1″; C-3″	116.5[a]	6.65 d (8.0)	C-1″; C-3″
6″	130.3[b]	6.97 d (8.4)	C-9; C-4″	120.7	6.50 dd (8.0; 2.0)	C-9; C-3″; C-4″	120.6	6.50 dd (8.0; 2.0)	C-9; C-2″; C-4″
β-D-Xylosyl or glucosyl moiety									
1	104.1	4.28 d (7.8)	C-3	103.6	4.33 d (7.8)	C-3	103.2	4.34 d (7.7)	C-3
2	75.0	3.11 br t (8.3)		75.2	3.14 dd (9.0; 7.8)		75.2	3.19 br t (8.0)	
3	77.7	3.37 t (8.8)		78.0	3.32 dd (9.0; 7.5)		78.0	3.36 br t (8.8)	
4	71.6	3.56 m		71.6	3.28 m		72.0	3.35 m	
5	65.6	3.89 dd (11.3; 5.5)		77.8	3.26 ddd (9.5; 5.2; 2.3)		78.2	3.26 ddd (9.7; 5.3; 2.4)	
		3.25 dd (11.3; 10.5)							
6				62.8	3.86 dd (12.0; 2.3)		62.8	3.88 dd (11.8; 2.4)	
					3.69 dd (12.0; 5.2)			3.72 dd (11.8; 5.3)	

[a–c] Values with the same superscript in one column may be interchanged.

up to the limit of the solvent boiling point. Thereby, the protic solvent's indisputable impact on the stability of the α-dione *s-cis* conformer is well proved since the signals do not collapse, even at such elevated temperature.

Finally, instead of releasing the anticipated 3″-hydroxy-α-ericadione aglycone ($C_{21}H_{24}O_6$), mild acid hydrolysis of glucoside **9** led directly to a mixture of species in the ratio 2:1 ($C_{21}H_{22}O_5$ and $C_{21}H_{20}O_4$), corresponding most likely to the major 3,4-dehydrated product **10** or its tautomer and to its 6,7-dehydrated tautomer **11**.[17] Alike α-ericadione, both compounds were characterized in the GC–MS analysis by the lack of the molecular ion and the permanent base peak *m/z* 107 (hydroxybenzylium).[2,18,19]



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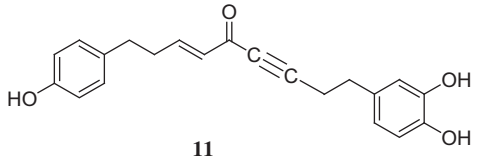

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The close relationship between all the *E. cinerea* 1,9-diarylnonanoids seems a priori to suggest a mutual 3-hydroxy-5,7-diketo-type precursor (β-ericadione) involved in two distinct pathways to lead mainly to open-chain metabolites and only secondarily to the partially cyclized 3,7-anhydro-6,7-dehydroericanone. The latter would most likely be issued from a route based on 6,7-enolisation followed by cylization consecutive to 3,7-dehydration. Conversely, the whole open long-chain group would be generated in four steps: a stereospecific reductive process of the 7-carbonyl leading to ericanone, then to 6,7-anhydroericanone after 6,7-dehydration, followed by 6,7-epoxidation and finally by rearrangement of the resulting α-epoxyketone to provide either α- and/or β-ericadione. In spite of a detailed phytochemical investigation of *E. cinerea* and to be consistent with this proposal, attempts to isolate the postulated β-ericadione and/or its keto-enol tautomer as well as the α-epoxyketone intermediate have remained unsuccessful.

Unlike more than 300 1,7-diarylheptanoids distributed in 15 less or more evolved plant families,[20] only 18 representatives of 1,9-diarylnonanoids are known. Up to now, they are restricted in the plant kingdom to the title *Erica* and the archaic *Myristica* (Myristicaceae) only, two genera far apart from each other on the plant evolution scale. The former contains two aglycones along with seven glycosides whereas the latter produces also a total of nine metabolites but only as aglycones.[1]

Acknowledgment

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3. *Isolation procedure:* The multistep chromatographic treatment of the previous crude EtOAc extract (50 g) subjected to LH-20 CC packed in MeOH gave the ahead fraction (4.9 g) reduced to 2.7 g after liquid–liquid partition with water. The organic fraction was then subjected to polyamide MPLC eluted with the mixture MeC_6H_5–Me_2CO–MeOH (from 80:10:10 to 60:20:20) to provide impure aglycones **1** and **5** in the ahead fractions and impure glycosides **2**–**4** and **6**–**9** in the last fractions. [1,2] Four fractions, issued from the previous step were, after the usual work-up, selected for isolating these glycosides. Besides surrounding absorbing materials for all, they were in the elution order, mainly consisting of mixed **6**–**8**, impure **9**, mixed **2**–**3**, and finally impure **4**. The latter glucoside (23 mg) was directly purified by reverse phase HPLC [Macherey–Nagel NUCLEODUR 100-5 C_{18} ec (250 × 10 mm)] with 45% aq. MeOH. Minor xyloside **3** (14 mg) was concentrated by repeated polyamide MPLC using a gradient of the mobile phase MeC_6H_5–Me_2CO–MeOH before being purified by three successive semi-prep. reverse phase C_{18} HPLC eluted with the mixture MeOH–H_2O (from 40:60 to 60:40). Glucoside **9** (65 mg) was finally subjected to direct semi-prep. reverse phase HPLC [Merck LiChrospher 100 DIOL (10 μm) 250 × 10 mm] with the eluent mixture *n*-C_6H_{14}–*i*PrOH–MeOH in the ratio 72:08:20.
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10. NMR signals with marked difference for the *s-cis* conformer of glucoside **9**: ^{1}H NMR (500 MHz, CD_3OD) δ: 4.16 (br quint, J = 6.5 Hz, H-3), 2.82 (dd, J = 16.8 and 7.0 Hz, H-4a), 2.72 (m, H_2-7), 2.64 (m, H-4b); ^{13}C NMR (125 MHz, CD_3OD) δ: 206.9 (C-6), 206.1 (C-5), 103.5 (C-1‴), 76.2 (C-3).
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16. *2,3-Pentanedione from Alfa Aesar:* ^{13}C NMR (100 MHz) δ ($CDCl_3$; 303 °K): 199.8 (C-3), 197.5 (C-2), 29.2 (C-4), 23.7 (C-1), 7.0 (C-5); δ (CD_3OD; from 303 °K up to 334 °K): 211.8 (C-3, *s-cis*), 209.8 (C-2, *s-cis*), 200.9 (C-3, *s-trans*), 198.7 (C-2, *s-trans*), 30.4 (C-4, *s-cis*), 29.8 (C-4, *s-trans*), 23.7 (C-1, *s-trans*), 23.4 (C-1, *s-cis*), 7.9 (C-5, *s-cis*), 7.3 (C-5, *s-trans*).
17. *Controlled acid hydrolysis of 3″-hydroxy-α-ericadione 3-glucoside* (**9**): The sample (8 mg) dissolved in MeOH (0.5 mL) was added to 3% HCl (10 mL). The mixture was kept for 2 h at 35 °C and then cooled. Diluted with distilled water (25 mL), the sample was extracted with EtOAc (3 × 10 mL). After the usual work-up, the residue was subjected to LH-20 CC packed in MeOH to afford a mixture (3 mg) of the major **10** and the minor **11**.
18. *3,4-Anhydro-3″-hydroxy-α-ericadione* (**10**): HRESMS for $C_{21}H_{22}NaO_5$ $[M+Na]^+$: calcd 377.155945, found 377.135982; HRESMS for $C_{21}H_{23}O_5$ $[M+H]^+$: calcd 355.154000, found 355.154038; GC-EIMS (70 eV) *m/z* (%): 208 (5), 190 (12), 147 (8), 133 (24), 107 (100), 91 (18), 77 (45), 65 (12), 43 (92).
19. *1-(4-Hydroxyphenyl)-9-(3,4-dihydroxyphenyl)-non-3-en-6-yn-5-one* (**11**): HRESMS for $C_{21}H_{21}O_4$ $[M+H]^+$: calcd 337.143436, found 337.143097; GC-EIMS (70 eV) *m/z* (%): 190 (5), 107 (100), 77 (25), 53 (5), 43 (43).
20. Lv, H.; She, G. *Nat. Prod. Commun.* **2010**, *5*, 1687–1708. and references cited therein.