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Chalcones and other constituents of *Dorstenia prorepens* and *Dorstenia zenkeri*

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Abstract

The twigs of *Dorstenia prorepens* furnished the digeranylated chalcone, 5,3′-(3,7-dimethyl-2,6-octadienyl)-3,4, 2′,4′-tetrahydroxychalcone while *Dorstenia zenkeri* yielded the 3′,4′-(3-hydroxy-2,2-dimethyldihydropyrano)-4,2′-dihydroxychalcone and a bichalcone. 4-Hydroxylonchocarpin was found in both plants. *D. prorepens* also yielded the known compounds: psoralen, bergapten, β-sitosterol and its D-glucopyranosyl derivative. *D. zenkeri* yielded *p*-hydroxybenzaldehyde, dorsmanin A, 4,2′,4′-trihydroxychalcone and 4,2′,4′-trihydroxy-3′-prenylchalcone. Structures of the new compounds were established by UV, IR, MS and 2-D NMR analysis. © 2002 Published by Elsevier Science Ltd.

Keywords: *Dorstenia prorepens*; *Dorstenia zenkeri*; Moraceae; Twigs; Leaves; Isolation; Geranylated chalcone; Prorepensin; Bichalcone; Diels–Alder adduct

1. Introduction

The genus *Dorstenia* Linne (Moraceae) is represented by 170 species worldwide (Mabberley, 1987). It is largely made up of undergrowth and herbaceous perennials with succulent and scrambling rhizomes (Berg et al., 1989). As part of our continuing program to study the chemical constituents of African *Dorstenia* species (Abegaz et al., 1998; Ngadjui et al., 1998a,b; 1999a,b, 2000), we have examined the extracts of the twigs of *D. prorepens* Engl and leaves of *Dorstenia zenkeri* Engl. To the best of our knowledge, no previous phytochemical studies have been reported on these species. This paper reports the isolation and structural elucidation of a new bis-geranylated chalcone, prorepensin (**1**), the known 4-hydroxylonchocarpin (**2**) (Dagne et al., 1989), psoralen (Kuster et al., 1994), bergapten (Swain et al., 1991; Kuster et al., 1994), β-sitosterol and its D-glucopyranoside from *D. prorepens*. From *D. zenkeri* the novel Diels–Alder derivative **3**, the hydroxydimethyldihydro pyrano derivative **8**, and the known dorsmanin A (**4**) (Ngadjui et al., 1998a), 4-hydroxylonchocarpin (**2**), 4,2′,4′-trihydroxychalcone (Barron and Ibrahim, 1996), 4,2′,4′-trihydroxy-3′-prenylchalcone (**5**) (Ngadjui et al., 1998a) and *p*-hydroxybenzaldehyde are reported. Known compounds were identified from spectroscopic and physical data and comparison with published information and / or with authentic specimens.

2. Results and discussion

Prorepensin (**1**) was isolated from the combined CH_2Cl_2/MeOH (1:1) and methanol extract of the dried powdered twigs of *D. prorepens* as described in Section 3. Its molecular formula was determined as $C_{35}H_{44}O_5$ from NMR and EIHRMS data. Its IR spectrum showed signals for a conjugated carbonyl and hydroxyl absorptions at ν_{max}1640 and 3450 cm^{-1}, respectively. The UV-visible absorptions at λ_{max} 268 and 389 nm were suggestive of a chalcone skeleton (Markham, 1982), which was confirmed by the ^1H NMR (see below). The bathochromic shift in the UV spectrum (Section 3) of compound **1** induced by $AlCl_3 + HCl$ indicated the

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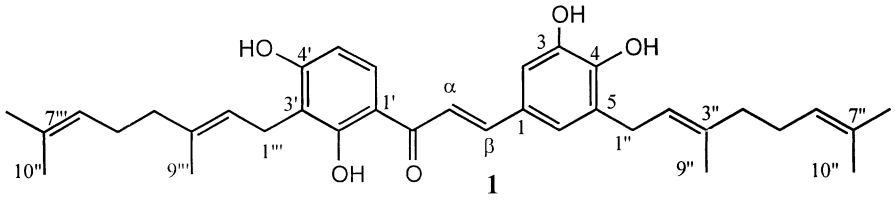

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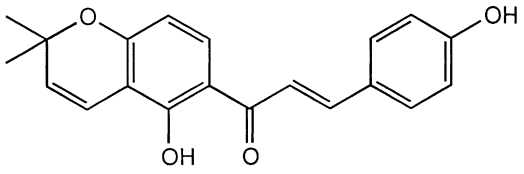

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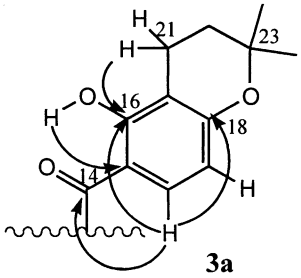
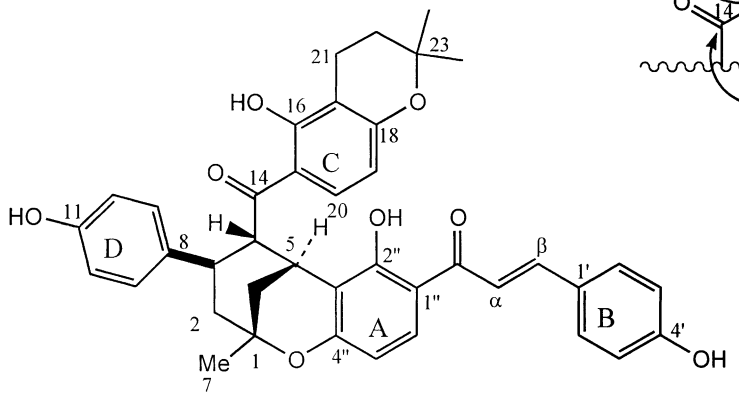


3a



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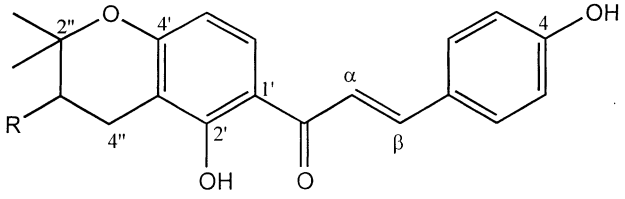
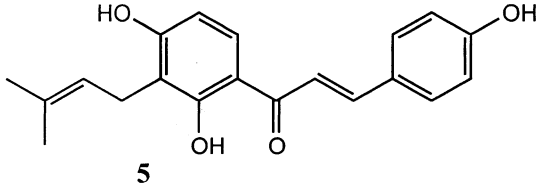


R = H
R = OH

4
8



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occurrence of free hydroxyl at 2′, and the shift induced by NaOAc suggested a second OH group at position 4′ (Mabry et al., 1970). The chelated hydroxyl proton signal appeared at δ 13.95 and a resonance at δ_C 192.6 for a chelated carbonyl group were consistent with a 2′-hydroxychalcone. The ^{13}C NMR spectrum of **1** displayed four oxygenated aromatic carbon signals. Two were assigned to the *ortho* dihydroxyl carbon s at δ144.8 (*s*) and 145.4 (*s*); the remaining signals at δ 162.2 (*s*) and 164.2 (*s*) are consistent with two oxygenated and *meta*-oriented carbons in a substituted benzene ring. The ^1H NMR spectrum of **1** showed signals for two geranyl groups: six vinyl methyl signals (see Table 1), four benzylic proton signals (δ_H 3.50 and 3.42), a broad singlet of eight protons at δ_H 2.12, and a pair of two broad triplets [δ_H 5.34 (2H) and 5.08 (2H)]. The low field region displayed only six proton resonance signals; two of them form an AB system at δ 7.42 and 7.77 (*d*,

$J = 15.4$ Hz), the large coupling constant indicating the *trans* geometry; a set of two signals at δ 6.43 and 7.72 each appearing as a doublet ($J = 8.9$ Hz), was also observed, which is assignable to the H-5′ and H-6′ protons of ring A, respectively. The multiplicities of the signals observed for these protons required that the 3′-position be substituted and one of the two geranyl groups was assumed to be located there. The remaining two broad singlets at δ 7.00 and 7.12 must, therefore, be due to two protons located in ring B. Detailed analysis of the ^{1}H and ^{13}C spectral data led to the initial assignment of the two *ortho* hydroxyl groups to C-3 and C-4 (^{13}C evidence) and the two singlets to H-2 and H-6. Since the COSY spectrum did not reveal any couplings between the two protons it was not possible to rule out a *para* disposition for them. Thus further evidence was required to decide between structure **1** and an alternative structure with the second geranyl group at C-2 and the two protons *para* to each other. Convincing proof for structure **1** was obtained from analysis of the HMBC spectrum which clearly showed correlation between H-2, H-6 and C-β signals and also interaction between the H-1″, C-4 and C-6 signals. The HMBC data also enabled the assignment of the signal at δ 7.00 to H-6 (and not to H-2) since it was the signal that displaced long range correlation with the C-1″ signal at δ 30.0 (see Table 2).

From the foregoing data prorepensin (**1**) is identified as 5,3′-digeranyl-3,4,2′,4′-tetrahydroxychalcone. The carbon resonances were assigned using DEPT, HMQC and HMBC. ^{13}C and ^{1}H NMR data are given in Table 1 and HMQC and HMBC are shown in Table 2. Finally, it was possible to determine the conformation of the compound with respect to the chalcone double bond. Two *trans*- arrangements are possible. The first is the linear structure shown in **1**. The second is an angular conformation which would orient the β-proton close to H-6′. Selective NOESY experiments were performed by irradiating both the α- and β-proton signals and it was found that only irradiation of the former resulted in the nuclear Overhauser enhancement of the H-6' signal. This result is consistent with the conformation of the chalcone as shown in **1** in the NMR solvent used.

Survey of the chemical literature reveals that bis-geranylated chalcones have not been reported so far. However, over ten chalcones containing one geranylated substituent have been reported in the literature. These include 4′-geranyloxy-4, 2′-dihydroxy chalcone (Dagne et al., 1990) from *Mellettia ferruginea* (Fabaceae), poinsettifolin B (Tsopmo et al., 1998) from *Dorstenia poinsettifolia* (Moraceae), flemingins A-F (Barron and Ibrahim, 1996) from *Flemingia rhodocarpa* and *F.congesta* (Fabaceae), flemiwallichin A-F (Barron and Ibrahim, 1996) from *Flemingia wallichii* (Fabaceae), boesenbergins A and B from *Boesenbergia pandura* (Zingiberaceae) and xanthoangelols A and B (Barron and Ibrahim, 1996; Hano et al., 1989) from *Angelica keiskei* (Apiaceae). To the best of our knowledge, prorepensin (**1**) is the first member of digeranylated chalcone.

The chloroform soluble portion of the organic extract of *D. zenkeri*, after flash chromatography, gel filtration on Sephadex LH-20 and subsequent purifications yielded seven compounds, two of which (**3** and **8**) are novel. Compound **3** was obtained as yellow oil and its molecular formula was determined as $C_{40}H_{38}O_8$ from HREIMS and NMR spectral measurements. The IR spectrum indicated the presence of carbonyl and OH

Table 1
NMR assignments of compound **1** in $CDCl_3$. Chemical shifts are given in ppm; multiplicities and coupling constant *J* (parentheses) in Hz

C/H	δ_C	δ_H	C/H	δ_C	δ_H
1	127.9 (*s*)	–	6″	124.1 (*d*)	5.08 (*m*)
2	112.9 (*d*)	7.12 (*br s*)	7″	132.7 (*s*)	–
3	144.8 (*s*)	–	8″	26.2 (*q*)	1.70 (*br s*)
4	145.4 (*s*)	–	9″	16.7 (*q*)	1.84 (*br s*)
5	128.1 (*s*)	–	10″	18.2 (*q*)	1.63 (*br s*)
6	124.1 (*d*)	7.00 (*br s*)	1‴	22.1 (*t*)	3.50 (*d*, $J = 7.1$)
β	145.0 (*d*)	7.77 (*d*, $J = 15.5$)	2‴	121.4 (*d*)	5.34 (quintet like *m*, $J = 7.1$)
α	118.5 (*d*)	7.42 (*d*, $J = 15.4$)	3‴	140.1 (*s*)	–
β′	192.6 (*s*)	–	4‴	40.1 (*t*)	2.12 (*m*)
1′	114.4 (*s*)	–	5‴	26.7 (*t*)	2.12 (*m*)
2′	164.2 (*s*)	–	6‴	124.0 (*d*)	5.08 (*m*)
3′	114.4 (*s*)	–	7‴	132.5 (*s*)	–
4′	162.2 (*s*)	–	8‴	26.1 (*q*)	1.69 (*br s*)
5′	108.3 (*d*)	6.43 (*d*, $J = 8.9$)	9‴	16.7 (*q*)	1.80 (*brs*)
6′	129.7(d)	7.72 (*d*, $J = 8.9$)	10‴	18.1 (*q*)	1.61 (*brs*)
1″	30.0 (*t*)	3.42 (*d*, $J = 7.1$)	2′-OH	–	13.95 (*brs*)
2″	121.5 (*d*)	5.34 (quintet like *m*, $J = 7.2$)			
3″	140.0 (*s*)	–			
4″	40.1 (*t*)	2.12 (*m*)			
5″	26.8 (*t*)	2.12 (*m*)			

groups as well as aromatic C–C carbon and Ar-CH bonds. The ^{13}C NMR, particularly DEPT analysis clearly established the presence of 40 carbons consisting of 17 methines, four methylenes, three methyl groups and 16 quaternary carbons. The ^{1}H NMR data displayed two signals at δ 13.63 and 13.89 indicating the presence of two chelated OH groups in the molecule. The aromatic region of the ^{1}H NMR spectrum showed signals representing 14 aryl/vinyl hydrogens, that were easily assigned to one *trans*-substituted double bond (2H), two *para*-substituted phenyl rings (B and D, 8H) and two sets of *ortho*-coupled protons contained in two tetra-substituted phenyl rings (A and C, 4H).

The chemical shifts of each of the two *ortho*-coupled protons (6.19 and 7.55 for the pair in C and, 6.42 and 7.75 for the set in A) suggested their dispositions to be β and γ to the two, respective, carbonyl groups. The value of the chemical shifts of these carbonyl groups at δ_C 208.5 and 192.4 suggested that the former one is not conjugated. The proton NMR spectrum of **3** also showed two triplets of two protons each at δ 2.69 and 1.81 together with a six-proton signal, which is consistent with the presence of a 2, 2-dimethyldihydropyran ring. The signals observed for this dimethyldihydropyran ring and for the chelated OH (δ 13.63) together with those for two *ortho*-coupled protons (δ 6.19 and 7.55) and for the carbonyl group at δ_C 208.5 were consistent with the partial structure **3a**. **3a** was confirmed by making use of the HMBC correlations.

The second set of *ortho*-coupled protons and the other chelated OH were now assumed to belong to the second tetra-substituted aromatic group. It was only after a thorough examination of the HMBC, COSY, TOCSY, and NOESY data that the gross structure of **3** was arrived at. Its ^{1}H, ^{13}C NMR and important HMBC correlation data are given in Table 3. TOCSY experiments were utilized to identify the various mutually coupled protons around the bicyclic system. A one-dimensional experiment using a Bruker pulse program selmlgp and a spin locking time of 250 ms provided a partial spectrum showing transfer of magnetization from H-4 to H-3, H-2a, H-2b and H-5. The signal of H-5 was stunted suggesting a weak coupling of H-4 to H-5. This was not surprising since the signal of H-4 appears as a doublet at δ 3.81 ($J = 9.1$ Hz) due to coupling to H-3 only. A second system was observed involving the signals of H-4, H-5, H-6a and H-6b only. It was also possible to conduct ROESY experiments allowing magnetization transfer through NOE effects from H-20 to H-5 and H-4. As shown in Fig. 1, **3** is believed to be derived from the two chalcones **5** and **6** via a Diels–Alder cycloaddition reaction to give adduct **7**, and subsequent cyclization reaction to form the bicyclic ring. A second cyclization to form the dihydropyran ring may have taken place before or after cycloaddition reaction. It is interesting to note that compound **7** was recently reported from a sister genus *D. barteri* (Tsopmo et al., 1998). The cycloaddition could, in principle, lead to any one of two isomers, but the relative stereochemistry was deduced from extensive 2D NMR analysis which also enabled us to reject an alternative mode of cycloaddition which would give rise to **3b,** by reaction of the same

Table 2
Important HMQC and HMBC correlations observed for compound **1**. ^{1}J (from HMQC) and ^{2}J, ^{3}J-gradient from HMB correlations of **1**

δ_H	Position	^{1}J-correlated carbon	^{2}J, ^{3}J correlated carbons
13.95	2′-OH	–	192.6 (C-β′), 164.2(C-2′), 114.4(C-1′,C-3′)
7.77	H-β	145.0	192.6 (C-β′), 127.9(C-1), 124.1(C-6), 112.9)(C-2)
7.72	6′	129.7	192.6 (C-β′), 164.2(C-2′), 162.2(C-4′), 114.4(C-1′)
7.42	H-α	118.5	192.6 (C-β′), 127.9(C-1)
7.12	2	112.9	145.4 (C-4), 145.0(C-β), 144.8(C-3), 124.1(C-6)
7.00	6	124.1	145.4 (C-4), 145.0(-C-β), 127.9(C-1), 112.9(C-2), 30.0(C-1″)
6.43	5′	108.3	162.2 (C-4′), 129.7(C-6′), 114.4(C-1′, C-3′)
5.34	2″	121.4	40.1 (C-4″), 30.0(C-1″), 16.7(C-9″)
5.34	2‴	121.5	40.1 (C-4‴), 22.1(C-1‴), 16.7(C-9‴)
5.08	6″	124.1	132.7 (C-7″), 18.2(C-10″)
5.08	6‴	124.0	132.5 (C-7‴), 18.1(C-10‴)
3.50	1‴	22.1	164.2 (C-2′), 162.2(C-4′), 140.1(C-3‴), 121.4(C-2‴), 114.4(C-3′)
3.42	1″	30.0	145.4 (C(C-4), 140.0(C-3″), 128.1(C-5), 124.1(C-6),121.5(C-2″)
2.12	4″	40.1	140.0 (C-3″). 124.1(C-6″), 26.8(C-5″), 16.7(C-9″)
2.12	4‴	40.1	140.1 (C-3‴), 124.0(C-6‴), 26.8(C-5‴)
2.12	5″	26.8	140.0 (C-3″), 132.7(C-7″), 124.1(C-6″, 40.1(C-4″), 16.7(C-9″)
2.12	5‴	26.8	140.1 (C-3‴). 132.5(C-7‴), 124.1(C-6‴), 40.1(C-4‴)
1.84	9‴	16.7	140.0 (C-3″), 40.1(C-4′),
1.80	9‴	16.7	140.1 (C-3‴), 40.1(C-4″)
1.70	8″	26.2	132.7 (C-7″), 124.1(C-6″), 18.2(C-10″)
1.69	8‴	26.1	132.5 (C-7‴), 124.0(C-6‴), 18.1(C-10‴)
1.63	10″	18.2	132.7 (C-7″), 124.1(C-6″), 26.2(C-10″)
1.61	10‴	18.1	132.5 (C-7‴), 124.1(C-6‴), 26.1(C-10‴)

Table 3
^1H, ^{13}C NMR and important HMBC correlation data of compound **3**. Chemical shifts are given in ppm; multiplicities and coupling constant *J* (parentheses) in Hz

Position	δ_H (ppm)	δ_C (ppm)	HMBC correlated C
1	–	76.8 *s*	
2a	2,22 *brdd* (5.0, 15.1)	42.0 *t*	29.2, 52.3
2b	2.18 *brdd* (12.4, 15.0)	42.0 t	76.8
3	3.27 *brddd* (5.0, 9.2, 12.6)	38.3 *d*	
4	3.81 *d* (9.1)	52.3 *d*	29.0, 38.3, 112.4, 135.6, 208.5
5	3.47 *m*	29.0 *d*	76.8, 115.7
6a	2.47 *dd* (1.8, 13.8)	30.5 *t*	29.0, 115.7,
6b	1.62 *dd* (3.5,13.6)	30.5 *t*	76.8, 42.0, 29.0
7	1.64 *s*	29.2 *q*	30.5, 42.0, 76.8
8	–	135.6 *s*	
9, 13	6.92 *brd* (8.4)	116.4 *d*	
10, 12	6.57 *brd* (8.6)	115.6 *d*	135.6
11	–	154.3 *s*	
14	–	208.5 *s*	
15	–	112.4 *s*	
16-OH	13.63 *brs*	163.9 *s*	108.9, 112.4
17	–	108.9 *s*	–
18	–	161.4 *s*	
19	6.19 *d* (9.0)	109.4 *d*	108.9, 112.4
20	7.55 *d* (9.0)	130.9 *d*	161.4, 163.9, 208.5
21	2.69 *t* (6.8)	16.7 *t*	32.3, 76.1, 108.9, 161.4
22	1.81 *t* (7.0)	32.3 *t*	76.1
23	–	76.1 *s*	
24, 25	1.35 s	27.1, 27.3 *q*	76.1
1′	–	128.5 *s*	
2′, 6′	7.58 *brd* (8.4)	131.0 *d*	158.3, 144.4, 131.0
4′	–	158.3 *s*	
3′, 5′	6.91 *brd* (8.2)	128.7 *d*	154.2, 128.5
1″	–	113.5 *s*	
2″-OH	13.89 *brs*	163.9 *s*	113.5, 115.7
3″	–	115.7 *s*	–
4″	–	160.5 *s*	–
5″	6.42 *d* (9.0)	109.6 *d*	113.5
6″	7.75 *d* (9.1)	129.7 *d*	160.5, 163.9, 192.4
C=O	–	192.4 *s*	
α	7.48 *d* (15.4)	118.4 *d*	128.5, 144.4 192.4
β	7.85 *d* (15.4)	144.4 *d*	131.0, 192.4

diene with the dienophile in the reverse orientation. Of particular significance in support of the latter conclusion was the echo-anti-echo ROESY experimental evidence, which clearly showed enhancement of the H-20 as a result of interaction with the H-5.

Compound **8** was isolated as a light yellow oil. The ^1H NMR spectrum of **8** clearly showed its chalcone nature by displaying the characteristic *trans* double bond proton signals and the substitution patterns of its two rings were almost identical to those of dorsmannin A (**4**) recently isolated from *D. mannii* (Ngadjui et al., 1998a). What was noticeably different was the appearance of an ABX system of proton signals in the aliphatic region (Table 4), which were consistent with the presence of an hydroxyl group in the dimethyldihydropyran ring. Initially it was not clear whether the hydroxyl group was located at the 3″ or the 4″- position. But this was readily established from HMBC studies where the C-H proton signal of the oxymethine group was found to have a long range correlation with C-2″, C-4″ (^2J) and C-2″(Me)$_2$, C-3′ (^3J). Furthermore the two proton signals of the C-4″ showed correlations with the two oxygenated carbons at C-2″ and C-4′. From the foregoing compound **8** is identified as 3′, 4′-(3-hydroxy-2, 2-dimethyldihydropyrano)-4, 2′-dihydroxychalcone. It is tempting to speculate that compound **8** is an intermediate in the biosynthetic pathway leading to the formation of the diene **6**, which is required for the Diels-Alder reaction leading to the formation of compound **3** discussed above.

3. Experimental

3.1. General

Mps uncorr.; UV-visible: MeOH solution; IR: KBr disk; EI and HR MS: direct inlet 70 eV; ^1H and ^{13}C NMR ($CDCl_3$,CD_3OD) 600 or 300 and 150 or 75 MHz, respectively, with the residual solvent peaks as internal references. HMQC and HMBC experiments were performed with gradient enhancements. The ROESY experiment was conducted with echo anti echo, 250 ms mixing time.

3.2. Plant material

The twigs of *D. prorepens* and the leaves of *D. zenkeri* were collected from Makak in the Central Province and around Kribi in the South Province, respectively, of Cameroon. Mr. Paul Mezili, of the National Herbarium in Yaounde identified the plants. Voucher specimens (No 6138/SR for *D. prorepens* and 43992 for *D. zenkeri*) are deposited at the National Herbarium, Yaounde, Cameroon.

3.3. Extraction and isolation from D. prorepens

The air-dried twigs of *D. prorepens* were powdered (750 g) and successively macerated in CH_2Cl_2/MeOH (1:1) and MeOH for 24 and 2 h, respectively at room temp. Removal of the solvent from the combined extracts under reduced pressure yielded a dark green residue (35 g). Part of this extract (30 g) was subjected to column chromatography (silica gel 60, 120 g) and eluted with hexane followed by hexane–EtOAc mixtures, EtOAc and EtOAc–MeOH mixtures to give several fractions of 250 ml. Frs were monitored by TLC and ^1H NMR and similar frs were combined. Frs 1–11 (4 g), examined by TLC (hexane–EtOAc; 9:1) contained mainly mixtures of hydrocarbons and phytosterols. Recryst. of the combined frs gave β-sitosterol (25 mg).

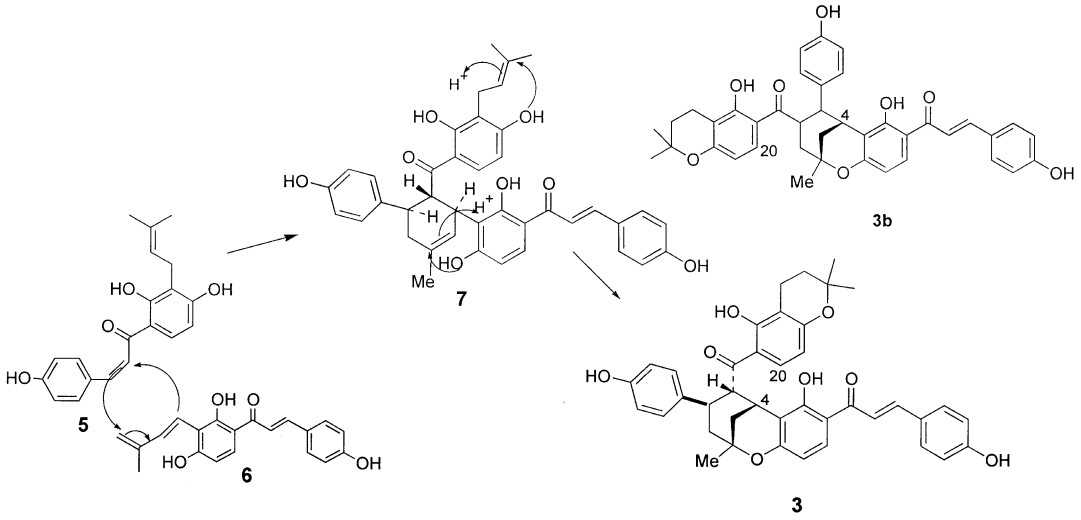

Fig. 1. Modified Diels–Alder adduct **3** arising from a diene and dienophile of two chalcones **5** and **6**.

Table 4
NMR assignments and important HMBC correlation data of compound **8** in methanol-d_4 Chemical shifts are given in ppm; multiplicities and coupling constant *J* (parentheses) in Hz

C/H	δ_C	δ_H	^2J and ^3J correlated carbons
1	127.3 *s*	–	
2, 6	130.2 *d*	7.53 *d* (8.7)	160.1, 142.2, 115.9
3, 5	115.9 *d*	6.85 *d* (8.6)	160.1, 127.3, 130.2
4	160.1 *s*	–	
1′	120.7 *s*	–	
2′	160.7 *s*	–	
3′	108.2 *s*	–	
4′	154.8 *s*	–	
5′	107.1 *d*	6.46 *d* (8.5)	120.7, 108.2
6′	130.0 *d*	7.49 *d* (8.6)	192.4, 160.7, 154.8
2″	77.9 *s*	–	
3′	68.6 *d*	3.85 *dd* (5.5, 7.0)	108.2, 24.9, 20.4
4″a	26.3 *t*	2.97 *dd* (5.5, 17.2)	160.7, 154.8, 108.2, 77.9, 68.6
4″b	26.3 *t*	2.64 *dd* (7.0, 17.2)	160.7, 154.8, 108.2, 77.9, 68.6
Me	24.9 *q*	1.42 *s*	77.9, 68.6, 20.4
Me	20.4 *q*	1.37 *s*	77.9, 68.6, 24.9
α	124.8 *d*	7.57 *d* (15.2)	192.4 142.2
β	142.2 *d*	7.59 *d* (15.4)	192.4, 130.2, 127.3
C=O	192.4 *s*	–	

Frs 12–16 (3 g) crystalized in the mixture of hexane-EtOAc to give psoralen (30 mg). Frs 17–40 (12 g) were passed through a Sephadex LH-20 column ($CHCl_3$/MeOH, 2:1). The post chlorophyll fraction was subjected, successively, to silica gel CC and PTLC to yield prorepensin (**1**, 25 mg), 4-hydroxylonchocarpin (**2**, 15 mg) and bergapten (20 mg). Frs 41–52 (1 g, hexane–EtOAc 2:3) contained mainly β-sitosterol-3-β-D-glucopyranoside. Known compounds were identified from spectroscopic and physical data and comparison with published information and/or with authentic markers.

3.4. Extraction, isolation from D. zenkeri

Likewise, the air-dried and powdered plant material of *D. zenkeri,* (2 kg) was extracted, successively, with a mixture of CH_2Cl_2–MeOH (1:1), MeOH and water at room temp. Removal of the solvent from the combined organic extract gave 120 g of residue. This residue was subjected to partition extraction with chloroform and ethyl acetate successively. The chloroform and ethyl acetate soluble fractions, after concentration in vacuo, yielded two dark green residues (80 and 15 g), respectively, which were combined on the basis of TLC analysis. The portion that was insoluble either in chloroform or in ethyl acetate (25 g), was found to contain mostly tannins and was not investigated further. Part (50 g) of the combined EtOAc and $CHCl_3$ soluble fractions was passed through Sephadex LH-20 column and eluted with a mixture of $CHCl_3$/MeOH (2:1). The post chlorophyll fraction (30 g) was subjected to silica gel (200 g) CC separations and eluted with CH_2Cl_2 followed by CH_2Cl_2-MeOH gradient. Fractions eluted with CH_2Cl_2 after repeated PTLC yielded: *p*-hydroxybenzaldehyde (7 mg), dorsmanin A (**4,** 20 mg), 4-hydroxylonchocharpin (**2**, 30 mg), 4,2′,4′-trihydroxy chalcone (15 mg) and 4,2′,4′-trihydroxy-3′-prenylchalcone (**5**, 40 mg). **3** (10 mg), **8** (8 mg) were obtained from repeated PTLC on fractions eluted with CH_2Cl_2-MeOH 98:2.

3.5. 5,3′-Digeranyl-3,4,2′,4′-tetrahydroxylchalcone, prorepensin (*1*)

Brown yellow oil; UVλ_{max}^{MeOH} log (ε): 268 (4.02), 389 (4.18); $\lambda_{max}^{MeOH+AlCl_3}$ mm log(ε): 290 (4.20), 330 (4.18), 344 (4.16), 432 (4.52); $\lambda_{max}^{MeOH+AlCl}3^{+HCl}$nm log($\varepsilon$): 288 (4.47), 330 (4.37), 406 (4.60), 430 (4.35); $\lambda_{max}^{MeOH+AlCl_3+HCl}$

nm log(ε) : 222 (4.80), 314 (474), 321 (4.62), 339 (4.62), 440 (4.75); IR ν_{max}^{KBr} cm^{-1} : 3450 (OH), 2920, 1640 (C=O), 1620, 1600, 1580, 1450, 1320, 1275; EIMS *m/z* (rel.int.): 544 $[M]^+$ (70), 529 $[M–Me]^+$ (10), 501 (20), 475[M-Prenyl]$^+$ (40), 459 (10), 422 (26), 393 (24), 273 (25), 271 (10), 203 (80), 149 (100); HR–EIMS: found: *m/z* 544.7251 M^+, $C_{35}H_{44}O_5$ requires: 544.7276; ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$): Table 1. HMQC and HMBC: Table 2.

3.6. Compound **3**

Yellow oil; $\alpha_D + 7.7^0$ (MeOH; c 1.3); UV λ_{max}^{MeOH} nm log(ε): 293 (4.58), 373 (4.74); $\lambda_{max}^{MeOH+AlCl_3}$ mm log(ε): 290 (4.60), 434 (4.78); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log(ε): no change; IR ν_{max}^{KBr} cm^{-1}: 3470 (OH), 3417 (OH), 1618, 1516, 1371, 1285, 1223, 1168, 1110 ; EIMS *m/z* (rel. int.%): 646 M^+ (46), 526 (8), 441 (38), 363 (10), 323 (14), 205 $[C_{12}H_{13}O_3]^+$ (74), 149 [205-C_4H_8]$^+$ (100), 120 (62); HR–EIMS: found: *m/z* 646.6723 M^+, $C_{40}H_{38}O_8$ requires: 646.6772; ^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$) and HMBC: Table 3.

3.7. 3′,4′-(3-Hydroxy-2, 2-dimethyldihydropyrano)-4,2′-dihydroxychalcone (**8**)

Yellow oil; $[\alpha]_D$ +31.3 (MeOH; c 0.32); UV λ_{max}^{MeOH} nm log (ε): 210 (4.80), 260 (4.78), 372 (4.80), $\lambda_{max}^{MeOH+AlCl_3}$ mm log (ε): 212 (4.81), 267 (4.72), 380 sh (4.70), 402 (4.68); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log (ε): 212 (4.80), 266 (4.73), 382 sh (4.74), 402 (4.70); IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1650 (C=O), 1610, 1560, 1500, 1480, 1360; EIMS m/z (rel. int.): 340 $[M]^+$ (100), 325 $M–Me^+$, 221 (40), 166 (25) 149 (20); HR–EIMS: found: *m/z* 340.3702.M^+, $C_{20}H_{20}O_5$ requires: 340.3730; ^{1}H NMR (600 MHz, CD_3OD), and ^{13}C NMR (150 MHz, CD_3OD): Table 4.

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