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HOSLUNDIN, HOSLUNDAL, AND HOSLUNDDIOL: THREE NEW FLAVONOIDS FROM THE TWIGS OF *HOSLUNDIA OPPOSITA* (LAMIACEAE)

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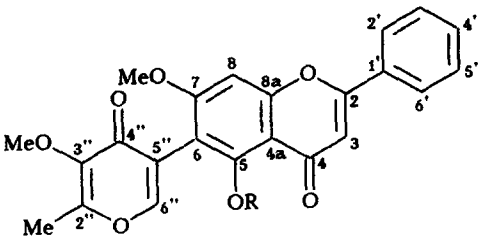
Abstract: Three new flavonoids (hoslundin **1**, hoslundal **4**, and hoslunddiol **6**) have been isolated from the twigs of *Hoslundia opposita*. The structure of hoslundin has been determined mainly by the use of 2D n.m.r. long-range δ_C/δ_H correlation in conjunction with the 1D proton-coupled ^{13}C n.m.r. spectrum, while the structures of the rest were established using ^1H and ^{13}C n.m.r. spectroscopy. The manner in which 2D n.m.r. long-range δ_C/δ_H correlation experiments are used for determining bond connectivity during the process of structural elucidation is discussed.

INTRODUCTION

Hoslundia opposita Vahl. is a small shrub which is widely distributed in West Africa.[1] Various parts of the plant are a popular remedy for *inter alia* snake bite, herpes, conjuctivitis, epilepsy, chest pain, yellow fever, stomach troubles, and mental disorders.[2] Infusions of its leaves have found wide use in traditional medicine as a purgative, diuretic, febrifuge, antibiotic, and antiseptic. The composition of the essential oil of *H. opposita* has been studied,[3] and crude extracts of the entire plant have been found to exhibit strong antibacterial activity.[4] Our interest in the systematic investigation of the chemical constituents of Cameroonian medicinal plants has led us to a chemical investigation of the twigs of *H. opposita*. This paper[5] reports the isolation and structural elucidation of three new flavonoids: hoslundin **1**, hoslundal **4**, and hoslunddiol **6**.

BOND CONNECTIVITY FROM 2D NMR LONG-RANGE δ_C/δ_H CORRELATION EXPERIMENTS

Flavonoids with several substituents are ideally suited to the structural elucidation strategy that we have previously developed and applied to ekeberginine (**7**)[6] and scapaniapyrone A (**8**).[7] This strategy involves combining information from the fully coupled ^{13}C spectrum and the 2D direct and long-range δ_C/δ_H correlation spectra; in most cases this procedure disposes of the need to undertake a large number of selective ^1H decoupling experiments on the ^{13}C spectra. When the fully coupled ^{13}C spectrum can be interpreted (in more complex cases a 2D heteronuclear J-resolved spectrum might provide the same information), then the long-range $^{13}C\cdots^1H$ coupling constants[8] and their assignments can provide valuable information about bond connectivity in situations where information from $^1H\cdots^1H$ coupling constants is lacking, *e.g.* around quaternary carbons or heteroatoms. Often it is possible to proceed without the knowledge of the values of the coupling constants and to decide bond connectivity on the basis of the 2D long-range δ_C/δ_H correlations alone. One simple but extremely effective application is the distinction of sites of ester attachment in compounds where several different esters are



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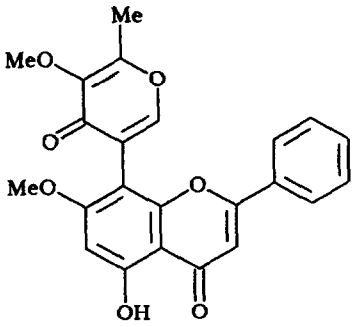
2 R = Me



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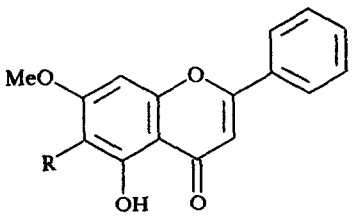
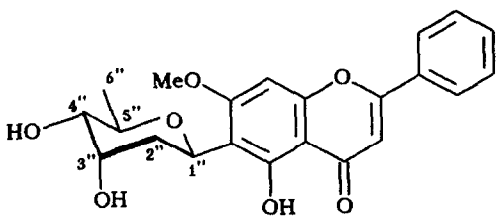


4 R = CH_2CHO
5 R = H



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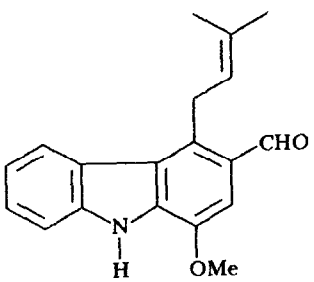

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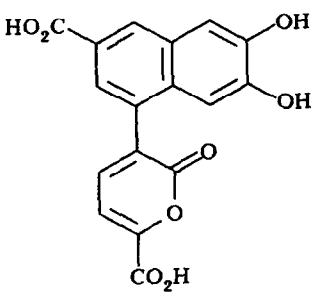

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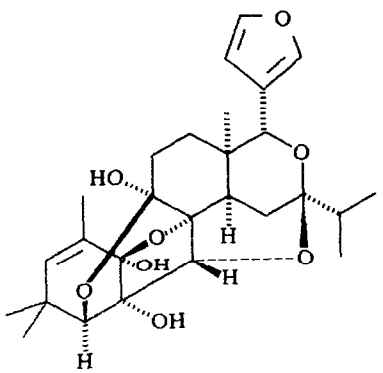

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present.[9] We have used this method extensively to study diterpenoids from *Euphorbia* species[10] and partially esterified sugars[11] where other methods are not only more difficult and time-consuming but also potentially ambiguous, *e.g.* when there is the possibility of transesterification during partial hydrolysis experiments.

One of the problems associated with using long-range $^{13}C/^{1}H$ correlations or couplings to make conclusions about structural connectivity is knowing how to deal with the possibility that either a two- or a three- bond interaction could be responsible for an observed correlation (it is usually assumed that four-bond couplings are too small to give rise to observable correlations with the parameters normally used). The numerical value of a coupling is often ambiguous in this respect.[8] One approach to this problem has been to develop pulse sequences that distinguish two- and three-bond $^{13}C\cdots^{1}H$ couplings directly, and in certain situations the XCORFE sequence[12] achieves this aim. Another possibility is, initially at least, only to utilise correlations where the coupling logically cannot be through two bonds.[13] One example already mentioned enables esters linkages to be defined; another situation, the correlation of the carbon of one tertiary methyl group to the protons of a second, enables a *gem*-dimethyl unit to be defined. Working in this manner makes it possible in favourable cases to elucidate even very complex structures from scratch, essentially without prejudice, as with the heptacyclic heptanortriterpenoid derivative entilin A (9).[14]

The pulse sequences used to measure long-range δ_C/δ_H correlations by 2D n.m.r. methods have evolved over the years. The original correlation sequence of Freeman and Morris[15] (with phase-cycling to achieve 'quadrature detection' in both dimensions[16]) when applied to long-range correlation suffers from the disadvantage that the one-bond ^{13}C–^{1}H coupling of proton-bearing carbons modulates the intensity of correlations from remote protons and can null these correlations.[17,18] A family of constant time experiments was developed as one way of overcoming this problem;[12,19,20] a concomitant effect was a reduction in flexibility and it became advisable before starting the acquisition of the 2D data set to optimize empirically the delays used. BIRD[21] and TANGO[22] pulse clusters were also introduced[20] to remove and counter the source of the intensity modulation, and were subsequently applied extensively[23] to the original correlation sequence. One sequence has so many BIRD pulses that it is known as FLOCK.[24] The pulse sequence[25] that we routinely use at the moment is essentially the same as sequence D reported independently by Krishnamurthy and Casida.[26] This incorporates a BIRD pulse cluster at the mid-point of the refocusing period of the original pulse sequence[15,16] and in addition uses TANGO excitation for the first proton pulse on the basis that it is beneficial to start the pulse sequence by generating transverse magnetization only from protons of interest, namely those attached to ^{12}C.

Some recent literature[23,24,27] has propounded that it is essential nowadays to use a pulse sequence that incorporates BIRD pulses to remove intensity modulation of long-range correlations. While we agree with this view in general, it is important to stress that conclusions drawn from results obtained using simpler pulse sequences are not necessarily

invalid. One of the main aims of using long-range correlations is to enable the structural elucidation argument to straddle quaternary carbon atoms; consequently much of the required information is derived by examining the resonances of the quaternary carbons themselves, and these are obviously unaffected by intensity modulation arising from directly bound protons. In this case the more complex pulse sequences confer no advantage and are arguably detrimental (on the basis that there is less opportunity for things to go awry in a short pulse sequence). Even in the case of proton-bearing carbon atoms it is only possible for the structural argument to come adrift if the absence of correlations is used to draw logical inferences. As ever it is preferable to use positive results rather than negative. In the present work the original pulse sequence[15,16] was used. Compound 2 contains relatively few protons and the fully coupled ^{13}C spectrum shows that, except in the phenyl group, none of the proton-bearing carbons are involved in long-range coupling; therefore nothing would be achieved by using a more complex pulse sequence.

RESULTS AND DISCUSSION

The methanolic extract of leafy twigs of *H. opposita* afforded, on repeated chromatographic separation and purification on silica gel, known sterols and triterpenoids (see Experimental), and in addition three new flavonoids: hoslundin 1, hoslundal 4, and hoslunddiol 6.

The first new compound, m.p. 287-288°C, $C_{23}H_{18}O_7$, is named hoslundin. Colour tests with magnesium - concentrated hydrochloric acid together with the u.v. spectral data (see Experimental) suggested that hoslundin is a flavone bearing a hydroxyl group at C-3 or C-5. The u.v. spectrum particularly resembled that of tectochrysin 5.[28] Since hoslundin readily gave a strong ferric chloride chelate reaction and showed a deshielded hydroxyl proton at δ_H 12.98 as well as the characteristic flavone H-3 signal (δ_H 6.58) in the n.m.r. spectrum, it is clear that it is a 5-hydroxyflavone. Diagnostic fragments at m/z 105 (15%) and 102 (16%) in the mass spectrum further defined the unsubstituted nature of the flavonoid ring B.

Most of the structural work was carried out on the monomethyl ether 2 of hoslundin. The combined use[6,7] of the fully coupled ^{13}C n.m.r. spectrum and the 2D δ_C/δ_H direct and long-range correlation spectra permitted the assignment of several part structures which can be assembled to give the flavonoid structure 2 for hoslundin methyl ether. The data are summarised in the Table. The carbon doublet at δ_C 153.2 has a $^1J_{CH}$ of 198.4 Hz with H_a and must be an enolic carbon. The carbonyl group at δ_C 173.6 couples to H_a and cannot be less than three bonds from this proton ($^3J_{CH}$ = 6.9 Hz). H_a also couples to carbons at δ_C 158.4 (J = 8 Hz), 122.0 (J = 6.8 Hz), and 113.0 (J = 2.5 Hz). These results are summarised in part structure 10 (the assignment of δ_C 113.0 to the carbon shown emerges later). The carbon at δ_C 158.4 is coupled to a methyl group (J = 7 Hz) which also couples (J = 3 Hz) with a carbon at δ_C 145.0 bearing a methoxyl group ($^3J_{CH}$ = 3 Hz). Thus the part structure 10 can be expanded to 11. The other possibility 12 is rejected as the double bond chemical shifts are in reverse order from that expected for this α,β-unsaturated enone structure, but are as expected for the pyrone structure in 11 (*cf.* maltol[29]). While there is no direct evidence for the closure of the ring to form a γ-pyrone there is no alternative once the flavonoid nucleus has been established.

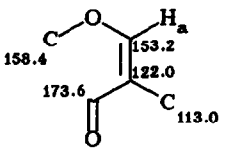
Table. ^{13}C and ^{1}H n.m.r. data (4.7 T) of *O*-methyl hoslundin 2.

Position	^{1}H label	δ_H	δ_C	$^{1}J_{CH}$	$^{2,3}J_{CH}$	Long-range correlations*
4			176.7		t (1.5)	(H_c), (H_b)
4"			173.6		d (6.9)	H_a
7			162.2		dq (3.5, 4.1)	H_b , 7-OMe
2			161.0		dt (4.9, 4.2)	H_c , ($H_{2',6'}$)
8a			159.6		d (5.1)	H_b
5			158.7		q (4)	5-OMe
2"			158.4		dq (8, 7)	H_a , 2"-Me
6"	H_a	7.64	153.2	198.4		
3"			145.0		sept (3)	3"-OMe, 2"-Me
1'			131.33		m*	H_c , $H_{3',5'}$ ‡
4'		7.49	131.27	161.8	t (7.5)	$H_{2',6'}$ ‡
3',5'			128.9	160	m	$H_{2',6'}$, $H_{4'}$
2',6'		7.87	125.9	160	m	$H_{4'}$
5"			122.0		d (6.8)	H_a
6			113.0		dd (5.7, 2.5)	H_b , (H_a)
4a			112.4		t (3.9)	H_b , H_c
3	H_c	6.66	108.8	166.5		
8	H_b	6.81	95.9	164.0		
5-OMe		3.72	62.3	145.6		
3"-OMe		3.87	59.9	144.9		
7-OMe		3.84	56.3	145.3		
2"-Me		2.37	14.7	130.1		

* Two experiments[14,15] were performed, with defocusing and refocusing periods 45 ms and 20 ms respectively and 80 ms and 40 ms respectively; correlations in parentheses were seen only in the experiment using the longer delays.

* This second-order multiplet has the appearance of a ddd with splittings of 3, 6, and 8 Hz. Selective decoupling of H_c removed the 3 Hz splitting.

‡ These attributions specifically to C-1' or C-4' are assumed; they could not be obtained directly as the digital resolution in the 2D experiments was insufficient to resolve C-1' and C-4'.



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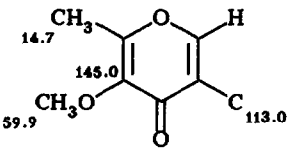

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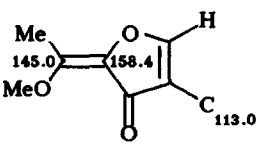

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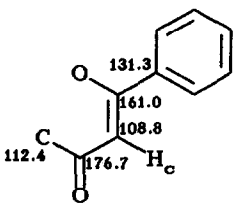
It is convenient to start the second unit with the phenyl group. The *ortho*-protons receive a NOE from the proton at δ_H 6.66 (H_c). In addition the *ortho*-protons couple to a carbon at δ_C 161.0 (^3J = 4.2 Hz) while H_c couples to C-1' (δ_C 131.3, ^3J = 3 Hz), to the carbonyl group at δ_C 176.7 (J = 1.5 Hz), and to a carbon (C-4a) at δ_C 112.4 (J = 3.9 Hz). These data can be summarised in part structure **13**, which constitutes part of the flavonoid nucleus indicated by the mass spectrum.



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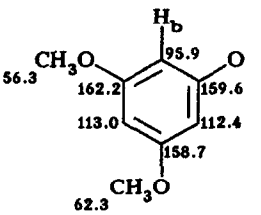

14

There are three remaining oxygen-bearing carbons of which two carry methoxyl substituents [δ_C 56.3 attached to δ_C 162.2 ($^3J_{CH}$ = 4.1 Hz) and δ_C 62.3 attached to δ_C 158.7 ($^3J_{CH}$ = 4 Hz)]; the third, δ_C 159.6, must be attached to the free oxygen in **13**. H_b (attached to δ_C 95.9, from the δ_C/δ_H direct correlation experiment) correlates with the free carbon in **13** at δ_C 112.4 (J = 3.9 Hz) as well as with δ_C 159.6 (J = 5.1 Hz). The latter coupling is assigned to a $^2J_{CH}$ in view of the 5-hydroxyl substituent in hoslundin deduced earlier; this assignment is consistent with our previous experience[7] that $^3J_{CH}$ of oxygen-bearing carbons is larger than 5.1 Hz. The methoxyl group at δ_C 56.3 has at least one *ortho* proton (methoxyl groups without neighbouring protons resonate nearer to 60 p.p.m.); this is confirmed by the production of a NOE at the proton resonance of this methoxyl group when H_b is irradiated. H_b also correlates (^3J = 5.7 Hz) with the free carbon at δ_C 113.0 in **11**. The methoxyl group at δ_C 62.3 is assigned to the methylated 5-hydroxyl substituent. These data, as shown in **14**, lead to the assignment of ring A of the flavonoid nucleus, and hence to structure **2** for hoslundin methyl ether.

During the isolation procedure hoslundin was always accompanied (t.l.c.) by a minor component. Efforts to isolate and characterise this compound were unsuccessful; it was apparently labile under the conditions used and we suspect that it was undergoing ready conversion into hoslundin **1**. It is known that 5-hydroxy-6-*C*-glycosyl flavones occur with the corresponding 8-*C*-isomers, and that the two isomers are interconverted by an acid-catalysed Wessely-Moser rearrangement.[30] It seems likely that the minor compound is the 8-*C*-isomer **3** of hoslundin **1** but we have no hard evidence to confirm this view. There are many references in the literature to pairs of 6-*C*- and 8-*C*-isomers occurring in 'equilibrium' with each other but only few indications of the relative stability. In the present case addition of one drop of trifluoroacetic

acid to a solution of 1 in $CDCl_3$ induced shifts in the ^1H n.m.r. spectrum, but this returned to normal when the acid was washed out by shaking the solution with an equal volume of water. Any equilibrium involving 1 and 3 appears therefore to lie essentially entirely in the direction of 1.

The second new compound, hoslundal 4, $C_{18}H_{14}O_5$, had absorption bands in its u.v. spectrum indicative of a flavone (λ_{max} 252, 265, 300 nm). A fragment ion at m/z 105 (20%) confirmed the presence of an unsubstituted ring B as in 1. The ^1H n.m.r. spectrum showed, *inter alia*, signals for one methoxyl group (δ_H 3.91), two isolated deshielded protons (δ_H 6.56 and 6.70), a chelated hydroxyl proton (δ_H 12.95), and a formylmethyl group [δ_H 3.75 (2H, br d, *J* 1.7 Hz); 9.68 (1H, t, *J* 1.7 Hz)]. These data suggested that hoslundal has structure 4 in which the pyrone moiety of hoslundin has been replaced by a formylmethyl group which presumably arose by degradation of the pyrone. The 6-formylmethyl structure is supported by the appearance of C-8 at δ_C 89.9, close to the value in swertisin;[31] the 8-formylmethyl isomer would be expected to show an equivalent signal (for C-6) around δ_C 95 as in isoswertisin.[31]

The third new flavonoid, hoslunddiol 6, (u.v. λ_{max} 252, 275, and 312 nm) was isolated from the more polar fractions of the methanolic extract of *H. opposita*. The mass spectrum revealed the molecular formula $C_{22}H_{22}O_7$ (m/z 398.1375) and the presence of an unsubstituted ring B [m/z 105 (27%) and 102 (10%)]. The ^1H n.m.r. spectrum of 6 was similar to that of the flavonoid portion of 1 or 4, and in addition there were signals for a *C*-glycosyl substituent. The chemical shifts and coupling constants of the sugar (see Experimental) led to the conclusion that it was a β-digitoxopyranose. The placing of this substituent at C-6 rather than C-8 again relies on the observation of a CH at δ_C 90 rather than near δ_C 95. The absolute configuration of the digitoxose moiety of 6 was established by application of the *in situ* method[32] of measuring the CD developed by glycols after bidentate binding to the complex $[Mo_2(OAc)_4]$. The complexed form shows a strong positive Cotton effect around 300 nm, characteristic for a positive torsional angle of the glycol unit. This is consistent only with the presence of D-digitoxose.[33] It is rare to find digitoxose attached to flavonoids.

The structure of hoslunddiol, 6-*C*-β-digitoxopyranosyltectochrysin 6, in which C-1 of digitoxose is attached directly to the aromatic A-ring of tectochrysin, is compatible with the accepted biogenetic derivation of these compounds. This is not the case with hoslundin 1 in which the 4-pyrone is attached through C-5". If 6 is a precursor of 1 then the attachment of the 4-pyrone to the aromatic ring A through C-5" rather than through the biogenetically expected C-6" position presumably involves the equivalent of a flavone - isoflavone rearrangement.[34]

EXPERIMENTAL

Melting points were measured on a Kofler hot stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer model 727B spectrometer, and the u.v. spectra on a Beckman model 25 grating spectrophotometer. N.m.r. spectra of $CDCl_3$ solutions were run at 25°C in the pulsed Fourier transform mode either on a Varian XL-100 spectrometer (25.16 MHz for ^{13}C, shifts relative to Me_4Si at δ0.00) or on a Bruker WP200SY spectrometer (200.13 MHz for ^1H, shifts relative to $CHCl_3$ at δ7.25; 50.32 MHz for ^{13}C, shifts relative to $CDCl_3$ at δ77.0). Mass

spectra were determined using a MS 902S instrument. Kieselgel 60 (0.063-0.200 mm, Merck) was used for column chromatography, and GF_{254} silica gel plates (0.5 mm thickness) were used for t.l.c..

Isolation of flavonoids from *Hoslundia opposita*.

Air-dried and powdered twigs of *H. opposita* Vahl. (2.45 kg) collected in June 1985 from Yaoundé, Central Province of Cameroon, were extracted with methanol (5 l) in a Soxhlet apparatus. The extract was concentrated under reduced pressure to 500 ml and acetone was added. Insoluble material was removed by filtration and the filtrate boiled under reflux with activated charcoal (3 h). Chromatography on celite and elution with acetone gave, after removal of the solvent, a dark green product (165 g). A sample (60 g) was dissolved in chloroform (20 ml) and chromatographed on a column of silica gel (800 g). Elution started with light petroleum and continued stepwise through light petroleum / ethyl acetate mixtures, ethyl acetate, and ethyl acetate / methanol mixtures. The eluate was collected in 250 ml fractions which were combined on the basis of t.l.c. comparisons using appropriate solvent systems. From this chromatographic separation euscaphic acid[35] (*syn.* acuminatic[36] or jacarandic[37] acid) (100 mg), a mixture (8.35 g) of oleanolic acid and ursolic acid, sterols (5.40 g) and their corresponding glucosides (2.50 g), and a mixture (6.30 g) of flavonoids and triterpenoids were obtained. G.l.c. of the sterols revealed a mixture of stigmastanol, stigmasterol, campesterol, and β-sitosterol. Further chromatographic separation and extensive preparative t.l.c. (chloroform/methanol 98/2) afforded pure hoslundin 1 (150 mg), hoslundal 4 (8 mg), hoslunddiol 6 (20 mg), and triterpene acids (3 g) in addition to a mixture (100 mg) of hoslundin 1 and (possibly) isohoslundin 3 which we failed to separate. The new flavonoids (hoslundin 1, hoslundal 4, and hoslunddiol 6) were characterized as follows.

Hoslundin 1 : Yellow needles, m.p. 287-288°C (hexane / ethyl acetate). λ_{max}(MeOH) (log ε) 250 (4.26), 273 (4.40), 312 nm (4.04); (MeOH + NaOMe) 253, 275 nm; (MeOH + $AlCl_3$) 252, 280, 330, 385 nm; (MeOH + $AlCl_3$ + HCl) 252, 280, 328, 383 nm; (MeOH + NaOAc + H_3BO_3) 248, 268, 310 nm. ν_{max} 3225, 1640, 1580, 1480, 1460, 1400, 1345, 1215, 1190, 1110, 1040, 900, 840, 800, 760 cm^{-1}. δ_H 2.37 (3H, s, Me-2"), 3.87 (3H, s, OMe), 3.90 (3H, s, OMe), 6.58 (1H, s, H-3), 6.69 (1H, s, H-8), 7.55 (3H, m, H-4', 2H-3',5'), 7.72 (1H, s, H-6"), 7.90 (2H, m, 2H-2',6'), 13.02 (1H, s, D_2O exch., 5-OH). δ_C (25 MHz) 182.3 (C-4), 173.3 (C-4"), 163.9 (C-2, C-7), 159.5 (C-8a), 158.2 (C-5, C-2"), 153.7 (C-6"), 145.2 (C-3"), 131.9 (C-4'), 131.2 (C-1'), 129.1 (2C-3',5'), 126.3 (2C-2',6'), 121.4 (C-5"), 106.1 (C-3), 105.8 & 103.8 (C-6 & C-4a), 90.3 (C-8), 60.0 (3"-OMe), 56.4 (7-OMe), 14.7 (2"-Me). M/z (rel. int.) 406 (M^+) (43), 392 (28), 391 $(M-CH_3)^+$ (100), 291 (25), 263 (36), 105 (15), 102 (16). Found: M^+ 406.1062; $C_{23}H_{18}O_7$ requires 406.1052.

***O*-methylhoslundin 2** : Diazomethane in ether was added to a solution of hoslundin 1 (20 mg) in methanol (3 ml) at room temperature; after 30 min. the solvent was evaporated. *O*-methylhoslundin 2 (18.5 mg) crystallized from methanol as colourless needles, m.p. 249-251°C. ν_{max} (KBr) 1640, 1580, 1450, 1425, 1360, 1340, 1250, 1220, 1100, 1010, 940, 870. δ_H 2.37 (3H, s, Me-2"), 3.72 (3H, s, 5-OMe), 3.84 (3H, s, 7-OMe), 3.87 (3H, s, 3"-OMe), 6.66 (1H, s, H-3), 6.81 (1H, s, H-8), 7.49 (3H, m, H-4', 2H-3',5'), 7.64 (1H, s, H-6"), 7.87

(2H, m, 2H-2',6'). δ_C : see Table. M/z (rel. int.) 420 (M^+) (66), 378 (49), 377 (M - CH_3 - CO)$^+$ (100), 349 (377 - CO)$^+$ (35), 335 (54), 334 (39), 307 (87), 306 (46), 291 (44), 105 (40), 102 (26). Found : M^+ 420.1204; $C_{24}H_{20}O_7$ requires 420.1209.

Hoslundal 4 : Yellow oil. λ_{max} (MeOH) 252, 265, 300 nm; (MeOH + NaOMe) 248, 270 nm; (MeOH + $AlCl_3$) 250, 275, 330, 384 nm. δ_H 3.75 (2H, d, *J* 1.7 Hz, CH_2CHO), 3.91 (3H, s, OMe), 6.56 (1H, br. s, H-8), 6.70 (1H, s, H-3), 7.54 (3H, m, H-4', 2H-3',5'), 7.90 (2H, m, 2H-2',6'), 9.68 (1H, t, *J* 1.7 Hz, CH_2CHO), 12.95 (1H, s, D_2O exch., 5-OH). δ_C (50 MHz; the S/N attained was poor and not all resonances were observed) 199.5 (CH_2CHO), 131.9 (C-4'), 131.3 (C-1'), 129.1 (2C-3',5'), 126.3 (2C-2',6'), 106.1 (C-3), 89.9 (C-8), 56.2 (OMe), 37.4 (CH_2CHO). M/z (rel. int.) 282 (M - CO)$^+$ (71), 281 (43), 253 (15), 252 (18), 251 (19), 105.0334 (20, C_7H_5O), 55.0182 (100, C_3H_3O). Found : (M - CO)$^+$ 282.0890; $C_{17}H_{14}O_4$ requires 282.0892.

Hoslunddiol 6 : Yellow needles, m.p. 192-193°C (chloroform/methanol). λ_{max} (MeOH) (log ε) 252 (4.17), 275 (4.38), 312 nm (4.08); (MeOH + NaOMe) 248, 274 nm; (MeOH + $AlCl_3$) 254, 284, 328, 385 nm. ν_{max} (KBr) 3450-3400, 1655, 1615, 1590, 1450, 1380, 1205, 1170, 1115, 1075, 855 cm^{-1}. δ_H 1.32 (3H, d, *J* 6.2 Hz, 3H-6"), 1.81 (1H, ddd, *J* 14, 3, 2 Hz, H-2"α), 2.93 (1H, ddd, *J* 14.3, 12.1, 2.5 Hz, H-2"β), 3.43 (1H, dd, *J* 9.5, 3.0 Hz, H-4"), 3.83 (1H, dq, *J* 9.5, 6.2 Hz, H-5"), 3.90 (3H, s, OMe), 4.21 (1H, q, *J* 3 Hz, H-3"), 5.45 (1H, dd, *J* 12.1, 2.0 Hz, H-1"), 6.47 (1H, s, H-8), 6.64 (1H, s, H-3), 7.51 (3H, m, H-4', 2H-3',5'), 7.88 (2H, m, 2H-2',6'), 13.23 (1H, s, D_2O exch., 5-OH). δ_C 182.7 (C-4), 164.3 & 163.8 (C-2 & C-7), 160.8 & 157.6 (C-5 & C-8a), 131.9 (C-4'), 131.4 (C-1'), 129.2 (2C-3',5'), 126.4 (2C-2',6'), 111.8 (C-6), 106.1 (C-3), 106.0 (C-4a), 90.3 (C-8), 73.4, 72.7, 68.3, 65.2 (C-1", 3", 4", 5"), 56.2 (OMe), 34.9 (C-2"), 18.6 (C-6"). M/z (rel. int.) 398 (M^+) (11), 354 (13), 339 (28), 335 (14), 297 (41), 295 (100), 294 (36), 293 (47), 281 (37), 279 (46), 239 (26), 105 (27), 102 (10). Found : M^+ 398.1375; $C_{22}H_{22}O_7$ requires 398.1365.

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