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Circular Dichroism of Sesquiterpene-Umbelliferone Ethers and Structure Elucidation of a New Derivative Isolated from the Gum Resin "Asa Foetida"*

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The CD spectra of 16 naturally occurring sesquiterpene-umbelliferone ethers, including the complete set of farnesiferol A isomers with all acetates and 6-oxo-derivatives, are reported over the significant wavelength range of 350–200 nm. 11 compounds were isolated from an "Asa Foetida" sample and 5 further derivatives, already known as natural products, were obtained by acetylation or *Jones* oxidation. In addition, a new compound – kamolonol (**14**) – was isolated. Its structure is characterized by twofold methyl migration in the drimenol derived sesquiterpene moiety. ^{1}H-NMR, MS, IR, UV, and CD data of the new compound are discussed.

(Keywords: Chiroptical properties; Coumarins; Farnesiferol A and isomers; ^{1}H-NMR)

Circulardichroismus von Sesquiterpen-Umbelliferon-Ethern und Strukturermittlung eines neuen Derivates aus dem Gummiharz "Asa Foetida"

Es werden die CD-Spektren von 16 natürlich vorkommenden Sesquiterpen-Umbelliferon-Ethern, einschließlich Farnesiferol A mit allen Isomeren und allen Acetyl- bzw. 6-Oxo-Derivaten, im signifikanten Wellenlängenbereich von 350–200 nm beschrieben. Elf der Verbindungen wurden aus einem „Asa Foetida"-Präparat isoliert, fünf weitere bereits als Naturstoffe bekannte Derivate wurden mittels Acetylierung oder *Jones*-Oxidation synthetisiert. Zusätzlich konnte eine neue Verbindung – Kamolonol (**14**) – isoliert werden, dessen Struktur durch zweifache Methylgruppenwanderung im Drimenyl-Sesquiterpenanteil charakterisiert ist. Die Strukturermittlung erfolgte mittels spektroskopischer Methoden (^{1}H-NMR, MS, IR, UV und CD).

* Herrn Prof. Dr. *K. Schlögl* mit den besten Wünschen zum 60. Geburtstag gewidmet.

Introduction

In a recent study on the circular dichroism of naturally occurring sesquiterpene-coumarin ethers we have discussed the chiroptical properties of a number of isofraxidin-sesquiterpene ethers[1]. Later, further CD data on related isofraxidin (6,8-dimethoxy-7-hydroxycoumarin) ethers were reported[2,3]. Thus it was of interest to compare these data with the CD spectra of related umbelliferone (7-hydroxycoumarin) ethers. In contrast to the isofraxidin derivatives this group of compounds has been investigated extensively over the last 20 years[4–6]. However, with the exception of a study on the short wavelength band of farnesiferol A and its isomers[7], no CD data have been reported so far. No data on the other two or three weaker bands at longer wavelengths have been reported at all. We have now recorded the CD spectra of a representative set of sesquiterpene-umbelliferone ethers isolated from a sample of "Asa Foetida", a gum resin from *Ferula assa foetida* L. or other closely related species[8]. In addition to already known sesquiterpene-umbelliferone ethers one new compound of this type was isolated and its structure determined.

Results and Discussion

The ether extract of a sample "Asa Foetida 70% cum semine foenugraeci 30% pulvis"* yielded nine sesquiterpene-umbelliferone ethers with a bicyclic sesquiterpene moiety (**1**, **3**, **4**, **6**, **8**, **9**, **11**, **13**, and the new derivative **14**) and two compounds with an open chain sesquiterpene residue (**16** and **17**). The other compounds of interest, e.g. the acetates **2** and **7**, and the oxo-derivatives **5**, **10**, and **12**, were obtained by acetylation (Ac_2O) or oxidation (CrO_3) of the corresponding alcohol. However, these derivatives have already been isolated as natural products as well. The diketone **15**, obtained by *Jones*-oxidation of the new compound **14**, is no naturally occurring product but proved to be useful for the structure elucidation of **14**.

Circular Dichroism

The two long wavelength transitions are located in the umbelliferone chromophore which is connected to a chiral sesquiterpene moiety by an ether bond. The two UV bands (usually at ca. 324 nm, $\varepsilon = 15\,000$ and 298 nm, shoulder with $\varepsilon = 9\,000$) are found in the CD spectra as well (see Table 1). For all bicyclic 6-hydroxy or 6-acetyloxy derivatives (**1–4**, **6–9**, **11**, and **13**) both *Cotton* effects corresponding to these UV absorptions are negative.

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* Kindly supplied by Siegfried Co. (Zofingen, Switzerland).

Table 1. *CD data for sesquiterpene-umbelliferone ethers* **1–17**

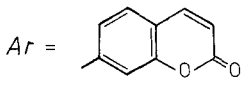
No.	CD Maxima (and Shoulders), *Et*OH, [nm($\Delta\varepsilon$)]				
1	321 (− 0.36)	292 (− 0.46)	252 (+ 0.30)	230 (− 1.25, sh)	205 (− 17.0)
2	320 (− 0.32)	295 (− 0.31)	240 (− 0.50, sh)		205 (− 14.2)
3	323 (− 0.71)	300 (− 0.45, sh)	245 (− 0.25, sh)	230 (− 0.35, sh)	205 (− 16.5)
4	320 (− 0.33)	295 (− 0.25, sh)		225 (− 0.90, sh)	203 (− 11.0)
5	330 (− 0.42)	295 (+ 0.05)	245 (− 0.50)	217 (− 1.9, sh)	203 (− 19.5)
6	323 (− 0.48)	285 (− 0.11, sh)	248 (− 0.50)	222 (− 1.5)	204 (− 5.3)
7	325 (− 0.75)	295 (− 0.37)			203 (− 3.8)
8	320 (− 0.83)	290 (− 0.40)		224 (− 1.0, sh)	204 (− 4.5)
9	323 (− 0.95)	295 (− 0.55, sh)		222 (− 1.45, sh)	205 (− 5.2)
10	330 (− 0.50)	295 (± 0.0)			204 (− 4.5)
11	324 (− 1.57)	303 (− 1.05, sh)	247 (− 1.2)	220 (− 1.3, sh)	
12	328 (− 0.58)	295 (+ 0.04)		235 (− 0.5, sh)	203 (− 10.3)
13	325 (− 0.40)	275 (− 0.40)	242 (− 0.40)	221 (+ 0.87)	
14	330 (− 0.42)	294 (+ 1.60)			
15	326 (− 1.20)	290 (+ 3.10)			
16	330 (− 0.22)	302 (+ 0.07)	262 (+ 0.08)	215 (+ 0.60, sh)	
17	328 (+ 0.36)	297 (− 0.25)	258 (− 0.45, sh)	218 (− 0.85, sh)	205 (− 10.8)

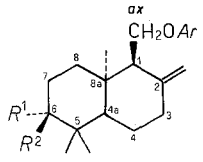
Comparison with the CD data of isofraxidin analogs show that no convincing correlation is possible for these bands. The long wavelength transition at ca. 324 nm for umbelliferones and ca. 337 nm for isofraxidins shows a weak negative *Cotton* effect for several 2-exo-methylene sesquiterpene-isofraxidin derivatives as well[1] (e.g. the isofraxidin analogs to **3**[9], **4**[9], **8**[2], **9**[10]). The transition at about 300 nm (which is the dominant UV maximum in isofraxidin derivatives but only a relatively weak shoulder for umbelliferone derivatives) does not correlate at all for the two series; e.g. **3** with effects at 323 nm ($\Delta\varepsilon = -0.7$) and 300 nm (sh, −0.45) compared with the isofraxidin analogue pectachol[1,8] with *Cotton* effects at 340 nm (−0.08) and 296 (+0.54) or its acetate[1,9] with effects at 345 (−0.08) and 295 (−0.36). In acetylpectachol[1,9] the sign of the effect at 295 nm is determined by the acetyl-carbonyl transition leading to inversion of the sign compared to the parent alcohol. This behaviour is found for *all* axial acetyl derivatives in the isofraxidin series, but *not* in the umbelliferone series.

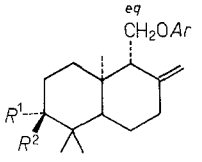
The only conclusion to be drawn is that the two methoxy groups adjacent to the ether bond in the coumarin moiety change the chromophor system and possibly the conformation relative to the sesquiterpene rest considerably. Both effects, the change in polarisation (reflected already in the different UV pattern for both series) *and* the change of the geometry by 6,8-dimethoxy substitution may contribute to the differencies in the CD

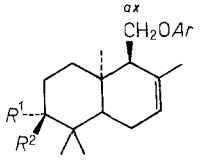
behaviour of the long wavelength region of the umbelliferone and isofraxidin series.

A different situation occurs within the short wavelength region dominated by CD transitions within the terpenoid moiety. The strong negative *Cotton* effect at ca. 205 nm for exo-methylene compounds of the umbelliferone series (**1**–**10**) is in the same order of magnitude for isofraxidin analogues as well: $\Delta\varepsilon$ between -15 and -20 for umbelliferone ethers with an axial $-CH_2OAr$ group and between -2 and -5 for an equatorial $-CH_2OAr$, compared to about -11 (ax $-CH_2OAr$) and -4 (eq $-CH_2OAr$) for the isofraxidin series[1–3]. The strong negative *Cotton* effects in the 2-exo-methylene compounds are indicative for an absolute configuration 4a *S*, 8a *R* for the substituted decaline system[1,7].









	R^1(eq)	R^2(ax)
1	OH	H
2	O*Ac*	H
3	H	OH
4	H	O*Ac*
5	=O	

	R^1(eq)	R^2(ax)
6	OH	H
7	O*Ac*	H
8	H	OH
9	H	O*Ac*
10	=O	

	R^1(eq)	R^2(ax)
11	OH	H
12	=O	

A second approach to correlate both coumarin series is possible by the transformation into the 6-keto compounds **5**, **10**, and **12**. In a previous paper on the CD of isofraxidin derivatives[1] it has been found that the 5,5-*gem.* dimethyl group causes an anti-octant behaviour of the A ring (this was observed for other similar compounds as well[11,12]). In the umbelliferone series this anti-octant trend is similar, although less pronounced than in the isofraxidin compounds. However, transformation of the alcohols **1** or **3** to the ketone **5**, **6** or **8** to **10**, and **11** to **12** results at least in an (anti-octant) increase of $\Delta\varepsilon$ at ca. 295 nm: **1**, **3** → **5** ($\Delta\varepsilon$ − 0.46, − 0.45 → + 0.05), **6**, **8** → **10** (− 0.11, − 0.4 → ± 0), and **11** → **12** (− 1.05 → + 0.04). In the isofraxidin series this anti-octant effect is more striking since already the alcohols have a positive *Cotton* effect at ca.

295 nm; the $\Delta(\Delta\varepsilon)_{\text{ketone-alcohol}}$ are in the order of $+0.5$ to $+1.0$, the $\Delta\varepsilon$ values are in the range of ca. $+1$ to $+2.5$ for the isofraxidin ketones (octant behaviour would require negative *Cotton* effects). This means that although the absolute values of the positive anti-octant *Cotton* effects are very small in the umbelliferone series (see Tab. 1) the relative changes are significant as well.

It seems of interest to note that **1**, **2**, and **11** have the most common 4a*S*, 8a*R* configuration, the isofraxidin analogs to these compounds (pectachol B, acetylpectachol B and drimartol B) were found to be of 4a*R*, 8a*S* configuration[1,3,9]. In all other known cases the isofraxidin and umbelliferone derivatives belong to the same absolute configuration (4a*S*, 8a*R*).

The new compound **14** (structure elucidation see below) exhibits a negative long wavelength *Cotton* effect, as *all* bicyclic *trans*-decaline type sesquiterpene-umbelliferone ethers of 4a*S*, 8a*R* configuration (**1**–**15**). The carbonyl transition at 294 nm is positive ($\Delta\varepsilon = +1.60$); this is again an anti-octant behaviour which might be caused either by strong sterical hindrance between the two equatorial substituents at C 4 and C 5 (OH and *Me* are very close) or, less probable, by an electronic interaction between the carbonyl group and the γ-hydroxy group[13,14].

Oxidation of **14** affords the diketone **15**. The latter shows a rather strong positive *Cotton* effect at 290 nm ($\Delta\varepsilon = +3.1$) which agrees with the proposed absolute configuration (4a*S*, 8a*R*) according to the octant rule with respect to the C4 carbonyl but not with respect to the C 6 carbonyl. However, predictions of absolute configurations from the CD spectra of diketones with polysubstituted and therefore strained cyclic structures are rather tentative since assumptions on possible conformations are uncertain (if not determined independently) and coupling phenomena of the two keto groups cannot be excluded.

The CD data of the two open chain sesquiterpene-umbelliferone ethers **16** and **17** are also presented in Table 1. However, any interpretation of the data would require more experimental material on closely related compounds.

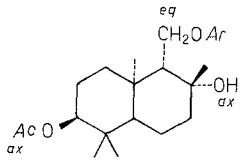
Structure Elucidation of Kamolonol (**14**)

The pattern of the aromatic resonance signals in the ^{1}H-NMR spectrum and the UV spectrum indicate clearly a umbelliferone derivative.

The dd (1 H, $J = 11$ and 4.5 Hz) at 3.96 and the rather sharp s (2 H) at 3.77 ppm indicate an equatorial secondary alcohol function (the H geminal to OH is axial, $J_{ax-ax} = 11$ Hz) and an equatorial $-CH_2OAr$ group (the protons in an axial $-CH_2OAr$ group should give clearly separated $-CH_2O-$ signals[9,10]). The singlet at 3.77 ppm (eq CH_2OAr) splits to a very narrow but clear AB system in C_6D_6; this is typical for sesquiterpene-coumarin ethers where the 8a-*Me* ax group has migrated to C 1 (in the usual derivatives, e.g. **1**–**12**, CH_2OAr represents the AB part of an ABX system). However, methyl *trans-trans* (ax → ax) migrations are rather common in several terpene and steroid series[15]. The four methyl groups of **14** are represented by two s and two d which are especially well separated in C_6D_6.

Decoupling (in C_6D_6, see Exp.) showed that the lowfield d (at 1.38 ppm) couples to a quartet at 2.00 ppm which is partially covered by other resonance signals. This q turns to a sharp s upon irradiation at 1.38 ppm, what means that the $-CH(CH_3)-$ group is flanked by two quaternary C. Assumption of a second methyl migration (*Me* 5 ax → *Me* 4a ax) and a carbonyl function at C 6 meet these requirements. The mass spectrum with $M = 398$ agrees with a bicyclic sesquiterpene-umbelliferone ether with one hydroxy and one carbonyl substituent and hydrogenation of the usual double bond in the B ring. The latter, in turn, agrees with the second methyl doublet in the ^{1}H-NMR spectrum (*Me* 2).

The sesquiterpene moiety of **14** contains therefore a saturated *trans*-decaline skeleton with two substituents at C 1 (*Me* ax and CH_2OAr eq), an axial *or* equatorial *Me* at C 2, an axial *Me* at C 4a, an equatorial *Me* at C 5, a keto function at C 6, and an equatorial OH at either C 7 *or* C 4. No other positions are possible for the hydroxy group because the H ax geminal to OH is represented by sharp dd which allows only a $>CH-CHOH-CH<$ or a C(quart.)$-CHOH-CH_2-$ arrangement; the former cannot be constructed at all, the latter is possible for a C 4 or C 7 hydroxy group.



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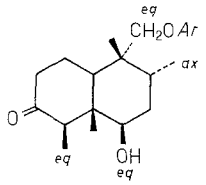
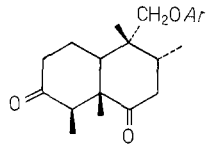


14



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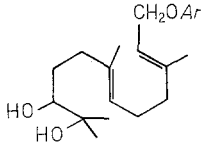

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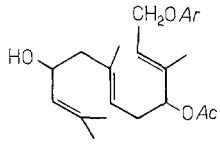

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The two open questions (*Me* 2 either ax or eq, OH eq either at C 4 or C 7) may be answered (i) by comparison with previously isolated isofraxidin-sesquiterpene ethers or (ii) by transformation of **14** into the diketo-compound **15**.

(i) Recently we have isolated two isofraxidin derivatives with a sequiterpene skeleton similar to **14**[16,17]: twofold methyl migration, a saturated B ring and a 6-oxo group; the *Me* at C 2 is either axial (in drimachone[16]) or equatorial (in isodrimachone[17]). However, these com-

pounds did not possess an additional hydroxy group. Comparison of the ^{1}H-NMR of drimachone, isodrimachone, and **14** allows some important conclusions:

a) *The H 7 eq resonance* (one of the few ring protons which were not obscured by other signals) *is almost identical for* **14** *and drimachone*[16] (ddd at 2.33 ppm with $J = 14, 5$, and 2.5 Hz for drimachone, 2.34 ppm and $J = 14, 4$, and 2 Hz for **14**) and still similar for isodrimachone (2.50 ppm, $J = 14$, 4, and 3 Hz). This seems important since it excludes position C 7 for the OH substituent (a 6-oxo-7-acetyloxy bicyclic sesquiterpene-isofraxidin ether has been already isolated[17], demonstrating that α-dioxygenated sesquiterpene residues are not unlikely in this series).

b) *The pattern of the methyl group signals of* **14** [1.18 (d), 1.12 (s), 1.10 (d), 0.85 (s), in $CDCl_3$] is matched reasonably well by drimachone [1.25 (d), 1.18 (s), 0.94 (d), 0.83 (s)] and not by isodrimachone [0.97 (d), 0.78 (s), 0.93 (d), 0.66 (s)].

c) *The pattern of the AB system for the methylene protons of the equatorial* $-CH_2OAr$ *group* at C 1 is again in favour of an axial *Me* at C 2. The shift differences for the two CH_2OAr protons are very small in the case of an axial *Me* 2 ($\Delta\delta = 0.04$ in $CDCl_3$ and 0.06 in C_6D_6 for drimachone) but appreciably larger for an equatorial *Me* 2 because of steric interaction between the equatorial $-CH_2OAr$ at C 1 and the equatorial *Me* at C 2 ($\Delta\delta = 0.12$ in $CDCl_3$ and 0.15 in C_6D_6 for isodrimachone). For **14** the corresponding values are $\Delta\delta \leqslant 0.02$ in $CDCl_3$ and 0.05 in C_6D_6.

Comparison of the available data therefore implies that in **14** the equatorial OH is positioned at C4 and that *Me* 2 is oriented axially.

(ii) The ^{1}H-NMR data of the diketo derivative **15** – obtained from **14** by *Jones*-oxidation – support these findings:

In case of a C 4 – OH group the corresponding 4,6-dioxo compound should possess a B ring with two protons α to the 4-carbonyl function; these protons should appear as the AB part of an ABC or, hopefully, an ABX system: $-CO-CH_2-CH(CH_3)-C$(quart.). Additionally, irradiation at the *Me* 2 doublet should reveal if the corresponding H 2 is axial or equatorial. However, again several of the decoupling experiments failed due to overlap of signals. Nevertheless, several conclusions may be drawn taking advantage from the few clearly assignable using either C_6D_6 or $CDCl_3$ as solvents.

a) In C_6D_6 two sharp dd are detectable in the aliphatic region: one at 2.02 ($J = 12$ and 3 Hz) and one at 2.49 ($J = 14$ and 5 Hz) [the latter one needs irradiation at 1.46 ppm (Me 5) for clear separation from the accidentally overlapping H 5 (see Exp.)]. The dd at 2.02 must be associated with an axial H, coupling with a vicinal H ax and a vicinal H eq; the latter protons cannot be in α-position to a carbonyl group since irradiation at 2.02 did not show any effect in the region of 1.6–2.5 ppm where this type of protons should be found. Keeping in mind the basic structure of the sequiterpene unit these conditions require a structural element $-CH_2-CH_2-CH(C\text{ quart.})_2$ which is *only possible for the 4,6-diketo compound.* The dd at 2.02 is assigned to the 8 a position, the dd at 2.49 ($J = 14$ and 5 Hz) can only be assigned to H 3.

b) In $CDCl_3$ the dd with $J = 14$ and 5 Hz (at 2.87 ppm) is clearly separated from all other resonances (the second dd with $J = 12$ and 3 Hz is covered by other signals and cannot be detected clearly). Irradiation of the dd at 2.87 results in the appearance of a distinct signal at 2.50 ppm emerging from a bulk of three protons. Unfortunately this signal is not clearly resolved because of overlap. However, $w_{1/2}$ is not larger than 7 Hz suggesting a small coupling constant. This agrees with the structure of a *4,6-diketone with an axial Me at C 2*: the signals at 2.87 and 2.50 represent the two H 3 protons as the AB part of an ABX system; the X proton (H 2) should be an equatorial one since both H 3 protons exhibit one large geminal and one small vicinal coupling ($H3_{eq}-H2_{eq}$ and $H3_{ax}-H2_{eq}$).

All arguments outlined in (i) and (ii) agree therefore fully with an axial *Me* 2 and an equatorial OH at C 4. A related compound (kamolon[15,18,19]) with twofold methyl migration, a 6-oxo function and an axial *Me* at C 2 has been reported previously. Originally a wrong structure was assigned to kamolon[18] which was revised later based on biogenetic arguments[15]. **14** is a hydroxy derivative of the revised structure of kamolon[15,19] with an axial OH at C 4. Kamolonol was therefore chosen as a trivial name for the new compound.

Acknowledgements

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Experimental Part

The CD spectra were recorded on a Jobin-Yvon Mark III (CNRS-Roussel-Jouan), for the NMR spectra a Bruker WM-250 spectrometer equipped with a 80 K Aspect computer was used. Optical rotations were determined on a Perkin-Elmer 241 polarimeter, IR spectra were taken on a Perkin-Elmer 398, and UV spectra on a Perkin-Elmer Lambda 5 instrument. Mass spectra were obtained on a Varian MAT CH-7.

Isolation of the Compounds: 2 g of a sample "Asa Foetida 70% cum semine foenugraeci 30% pulvis" were extracted for 10 h with 30 ml Et_2O at room temperature. The crude extract (ca. 150 mg) was separated by repeated prep. tlc (silica gel, Merck, ether/petrol ether 7:3). Material from the distinct blue fluorescent bands on the tlc plate were checked by NMR and further purified by repeated tlc (**3**, **8**, **14**, **16**) or separated into further components either by tlc (**13** from **17**, **4** from **9**, **11** from **1** + **6**) or on a cellulose acetate column at elevated pressure with ethanol as eluent (**1** from **6**; for details see[20]).

The above mentioned compounds were isolated from Asa Foetida, the acetates **2** and **7** and the oxo-derivatives **5**, **10**, **12**, and **15** were obtained as follows.

Acetylation: 1 mg of **1** or **6** was treated with 0.2 ml of acetic anhydride at 60° for 5 h. Evaporation of excess anhydride and prep. tlc afforded **2** or **7**, respectively.

Jones-Oxidation: 1 mg of **1**, **8**, **11** or **14** was stirred together with 10 mg CrO_3 in 0.5 ml of dry pyridine for 15 h at room temperature. Then 10 ml of ether and

enough 2 *n* HCl was added until the aqueous layer turned acidic. The ether layer was washed neutral, dried over $MgSO_4$ and the ether evaporated. The remaining oil was purified by tlc to give the compounds **5**, **10**, **12**, and **15**.

Characterization of the Compounds: The following list includes the trivial names with corresponding references, the yields from 2 g of Asa Foetida, the *Rf* values for Merck silica gel 60 F 254 (ether/petrol ether 9 : 1), and detailed ^{1}H-NMR data for the sesquiterpene moiety of the compounds; the umbelliferone part is almost identical for all compounds (± 0.01 ppm), the complete set of data for the new compound **14** is therefore considered representative with regard to the aromatic protons. Optical rotations were checked and were found to agree with literature data (see either original Refs. or reviews[4–6]).

1, *farnesiferol A*[21–24], 12 mg, *Rf* = 0.34; NMR ($CDCl_3$): 4.85 (br. s, 1 H, $w_{1/2}$ = 5 Hz, exo-methylene), 4.75 (br. s, 1 H, $w_{1/2}$ = 5 Hz, exo-methylene), 4.31 (dd, 1 H, *J* = 10.5 and 6 Hz, $-CH_2OAr$), 4.04 (dd, 1 H, *J* = 10.5 and 6.5 Hz, $-CH_2OAr$), 3.28 (dd, 1 H, *J* = 9 and 7 Hz, H 6), 2.35 (br. pseudo d, 1 H, $J_{gem.}$ = 13 Hz, H 3 eq), 2.23 (ps. t, 1 H, *J* = 6 and 6.5 Hz, H 1), 2.07 (ddd, *J* = 13, 13, and 4 Hz, H 3 ax), 1.69–1.77 (m, 3 H), 1.25–1.65 (m, 5 H), 1.06 (s, 3 H, *Me*), 1.00 (s, 3 H, *Me*), 0.82 (s, 3 H, *Me*).

2, *polyanthin* (poliantin)[25,26], by acetylation of **1**; NMR ($CDCl_3$): 4.85 (br. s, 1 H, exo-methylene), 4.75 (br. s, 1 H, exo-methylene), 4.52 (dd, 1 H, *J* = 9 and 7 Hz, H 6), 4.31 (dd, 1 H, *J* = 10.5 and 6 Hz, $-CH_2OAr$), 4.04 (dd, 1 H, *J* = 10.5 and 6.5 Hz, $-CH_2OAr$), 2.35 (br. ps. d, 1 H, $J_{gem.}$ = 13 Hz, H 3 eq), 2.23 (ps. t, 1 H, *J* = 6 and 6.5 Hz, H 1), 2.07 (s, 3 H, CO*Me*), 2.06 (m, H 3 ax), 1.2–1.8 (m, 7 H), 1.03 (s, 3 H, *Me*).

3, *gummosin*[22–24,27,28], 3 mg, *Rf* = 0.40; NMR ($CDCl_3$): 4.83 and 4.73 (two br. s, $w_{1/2}$ = 5–6 Hz, exo-methylene), 4.42 (dd, 1 H, *J* = 10 and 5 Hz, $-CH_2OAr$), 4.10 (dd, 1 H, *J* = 10 and 7 Hz, $-CH_2OAr$), 3.50 (br. s, 1 H, $w_{1/2}$ = 7 Hz, H 6), 2.35 (br. ps. d, 1 H, $J_{gem.}$ = 13 Hz, H 3 eq), 2.0–2.2 (m, 3 H, H 1 + H 8 ax^9 + H 3 ax), 1.80 (dd, 1 H, *J* = 13 and 3 Hz, H 4 a), 1.55–1.70 (m, 5 H), 1.45 (m, H 4 ax), 1.02 (s, 3 H, *Me*), 1.01 (s, 3 H, *Me*), 0.87 (s, 3 H, *Me*).

4, *polyanthinin* (poliantinin)[25,26], 3 mg, *Rf* = 0.71; NMR ($CDCl_3$): 4.84 and 4.74 (two br. s, exo-methylene), 4.71 (br. s, 1 H, H 6), 4.39 (dd, 1 H, *J* = 10 and 5.5 Hz, $-CH_2OAr$), 4.11 (dd, 1 H, *J* = 10 and 7 Hz, $-CH_2OAr$), 2.35 (br. ps. d, 1 H, $J_{gem.}$ = 13 Hz, H 3 eq), 2.0–2.2 (m, 3 H), 1.79 (dd, 1 H, *J* = 13 and 3 Hz, H 4 a), 1.5–1.7 (m, 4 H), 1.45 (m, H 4 ax), 1.03 (s, 3 H, *Me*), 0.93 (s, 3 H, *Me*), 0.92 (s, 3 H, *Me*).

5, *mogoltadone*[22,29], by oxidation of **1**; NMR ($CDCl_3$): 4.91 and 4.83 (two br. s, exo-methylene), 4.25 (dd, 1 H, *J* = 10.5 and 5 Hz, $-CH_2OAr$), 4.04 (dd, 1 H, *J* = 10.5 and 6 Hz, $-CH_2OAr$), 2.79 (ddd, 1 H, *J* = 15, 15, and 6 Hz, H 7 ax), 2.32 –2.42 (m, 2 H), 1.60–2.15 (m, 4 H), 1.21 (s, 3 H, *Me*), 1.14 (s, 3 H, *Me*), 1.05 (s, 3 H, *Me*).

6, *coladonin* (koladonin)[30,22–24], 2.5 mg, *Rf* = 0.33; NMR ($CDCl_3$): 4.95 and 4.57 (two br. s, 1 H each, $w_{1/2}$ = 4 Hz, exo-methylene), 4.18–4.23 (m, 2 H, $-CH_2OAr$), 3.31 (dd, 1 H, *J* = 11 and 5 Hz, H 6), 2.48 (ddd, 1 H, *J* = 14, 5, and 3 Hz, H 3 eq), 2.22 (dd, appears as a br. t, 1 H, *J* ca. 6.5/6.5 Hz, H 1), 2.10 (ddd, 1 H, *J* = 14, 13, and 4 Hz, H 3 ax), 1.20–1.85 (m, 8 H), 1.03 (s, 3 H, *Me*), 0.85 (s, 3 H, *Me*), 0.82 (s, 3 H, *Me*).

7, *coladin* (koladin)[30], by acetylation of **6**; NMR ($CDCl_3$): 4.94 (br. s, 1 H, exo-methylene), 4.56 (m, 1 H, H 6), 4.55 (br. s, 1 H, exo-methylene), 4.18–4.22 (m, 2 H, $-CH_2OAr$), 2.46 (m, 1 H, H 3 eq), 2.22 (m, 1 H, H 1), 2.10 (m, 1 H, H 3 ax), 2.07 (s, 3 H, CO*Me*).

8, *badrakemin*[31,32,22–24,28], 3.5 mg, $Rf = 0.43$; NMR ($CDCl_3$): 4.92 and 4.55 (two br. s, exo-methylene), 4.25 (dd, 1 H, $J = 11$ and 5 Hz, $-CH_2OAr$), 4.18 (dd, 1 H, $J = 11$ and 7 Hz, $-CH_2OAr$), 3.49 (br. ps. s, 1 H, $w_{1/2} = 7$ Hz, H 6), 2.48 (br. ps. d, 1 H, $J_{gem.} = 13$ Hz, H 3 eq), 2.35 (dd, appears as a br. ps. t, 1 H, $J = 5$ and 7 Hz, H 1), 2.16 (ddd, 1 H, $J = 13$, 12, and 4 Hz, H 3 ax), 1.6–2.0 (m, 6 H), 1.45 (m, 1 H, H 4 ax), 0.99 (s, 3 H, *Me*), 0.88 (s, 3 H, *Me*), 0.86 (s, 3 H, *Me*).

9, *badrakeminacetate*[33], 3 mg, $Rf = 0.70$; NMR ($CDCl_3$): 4.94 (br. s, 1 H, $w_{1/2} = 5$ Hz, exo-methylene), 4.72 (br. s, 1 H, $w_{1/2} = 7$ Hz, H 6), 4.56 (br. s, 1 H, $w_{1/2} = 5$ Hz, exo-methylene), 4.23 and 4.18 (narrow AB part of an ABX system, 2 H, J ca. 10/4 and 10/8 Hz, $-CH_2OAr$), 2.49 (br. ps. d, 1 H, $J_{gem.} = 13$ Hz, H 3 eq), 2.35 (br. ps. s, 1 H, $w_{1/2} = 16$ Hz, H 1), 2.17 (m, 1 H, H 3 ax), 2.09 (s, 3 H, CO*Me*), 1.6 –2.0 (m, 5 H), 1.46 (m, 1 H, H 4 ax), 0.93 (s, 3 H, *Me*), 0.90 (s, 3 H, *Me*), 0.88 (s, 3 H, *Me*).

10, *badrakemone*[34], by oxidation of **8**; NMR ($CDCl_3$): 4.98 and 4.62 (two br. s, exo-methylene), 4.21–4.25 (m, 2 H, $-CH_2OAr$), 2.70 (ddd, 1 H, $J = 15$, 15, and 6 Hz, H 7 ax), 2.30–2.50 (m, 2 H), 1.95–2.15 (m, 2 H), 1.55–1.75 (m, 2 H), 1.13 (s, 3 H, *Me*), 1.08 (s, 3 H, *Me*), 1.05 (s, 3 H, *Me*).

11, *foliferidin*[35], 1 mg, $Rf = 0.35$; NMR ($CDCl_3$): 5.58 (br. s, 1 H, $w_{1/2} = 10$ Hz, H 3), 4.19 (dd, 1 H, $J = 10$ and 3 Hz, $-CH_2OAr$), 4.03 (dd, 1 H, $J = 10$ and 5.5 Hz, $-CH_2OAr$), 3.31 (dd, 1 H, $J = 10.5$ and 6 Hz, H 6), 2.22 (m, 1 H), 1.98–2.06 (m, 2 H), 1.70 (br. s, 3 H, olefin. *Me*), 1.25–1.75 (m, 6 H), 1.01 (s, 3 H, *Me*), 0.92 (s, 3 H, *Me*), 0.90 (s, 3 H, *Me*).

12, synth. by oxidation of **11**; NMR ($CDCl_3$): 5.62 (br. ps. s, 1 H, $w_{1/2} = 10$ Hz, H 3), 4.18 (dd, 1 H, $J = 10$ and 4 Hz, $-CH_2OAr$), 4.08 (dd, 1 H, $J = 10$ and 5.5 Hz, $-CH_2OAr$), 2.77 (ddd, 1 H, $J = 15$, 15, and 6 Hz, H 7 ax), 2.27–2.40 (m, 2 H), 1.95–2.10 (m, 2 H), 1.73 (br. s, 3 H, olefin. *Me*), 1.50–1.70 (m, 2 H), 1.15 (s, 3 H, *Me*), 1.13 (s, 3 H, *Me*), 1.09 (s, 3 H, *Me*).

13, *samarcandinacetate*[36], 8 mg, $Rf = 0.30$; NMR ($CDCl_3$): 4.67 (br. s, 1 H, $w_{1/2} = 8$ Hz, H 6), 4.16–4.20 (m, 2 H, $-CH_2OAr$), 1.90–2.10 (m, 3 H), 1.80 (s, 3 H, CO*Me*), 1.30–1.80 (m, 6 H), 1.38 (s, 3 H, *Me*), 1.33 (s, 3 H, *Me*), 1.05–1.20 (m, 2 H), 0.96 (s, 3 H, *Me*), 0.92 (s, 3 H, *Me*).

14, *kamolonol*, 3.5 mg, $Rf = 0.24$, $[\alpha]_D^{20} = +17°$ and $[\alpha]_{436}^{20} = +35°$ ($c = 0.15$, $CHCl_3$); IR (CCl_4): 3 640, 3 615, 2 970, 2 860, 1 744 (vs), 1 712 (s), 1 612 (vs), 1 503, 1 347, 1 275 (s), 1 225 (s), 1 155, 1 120 (s), 1 022, 890 cm^{-1}; UV (*Et*OH): 322 (15 200), 296 (sh, 8 800), 251 (sh, 2 600), 240 (sh, 3 600), 215 (sh, 14 000), 205 (26 400); CD (*Et*OH): siehe Tab. 1; MS (70 eV, 130 °C): 398 (18), 219 (16), 165 (11), 163 (56), 162 (100), 147 (20), 135 (16), 134 (22), 133 (11), 123 (17), 121 (21), 119 (14), 111 (16), 109 (26), 107 (22), 105 (13), 97 (14), 95 (32), 93 (16), 91 (11); NMR ($CDCl_3$): 7.67 (d, 1 H, $J = 9.5$ Hz, umb. H 4), 7.40 (d, 1 H, $J = 9$ Hz, umb. H 5), 6.85 (dd, 1 H, $J = 9$ and 2.5 Hz, umb. H 6), 6.83 (d, 1 H, $J = 2.5$ Hz, umb. H 8), 6.27 (d, 1 H, $J = 9.5$ Hz, umb. H 3), 3.96 (dd, 1 H, $J = 11$ and 4.5 Hz, H 4), 3.77 (br. s, 2 H, $-CH_2OAr$), 2.45–2.60 (m, 2 H), 2.25–2.40 (m, 2 H), 2.12–2.20 (m, 2 H), 1.85–2.05 (m, 3 H), 1.50–1.75 (m, 2 H), 1.18 (d, 3 H, $J = 6.5$ Hz, *Me*), 1.12 (s, 3 H, *Me*), 1.10 (d, 3 H, $J = 7$ Hz, *Me*), 0.85 (s, 3 H, *Me*); NMR (C_6D_6): 6.66 (d, 1 H, $J = 9$ Hz, umb. H 5), 6.61 (d, 1 H, $J = 9.5$ Hz, umb. H 4), 6.54 (dd, 1 H, $J = 9$ and 2.5 Hz, umb. H 6), 6.52 (d, 1 H, $J = 2.5$ Hz, umb. H 8), 5.92 (d, 1 H, $J = 9.5$ Hz, umb. H 3), 3.49 (dd, $J = 11$ and 4.5 Hz, H 4), 3.20 and 3.15 (narrow AB system, 2 H, $J = 9$ Hz, $-CH_2OAr$), 2.34 (m, 1 H, $J_{gem.} = 14$ Hz), 1.85–2.10 (m, 3 H, including H 5 at 2.00), 1.15–1.70 (m, 6 H), 1.38 (d, 3 H, $J = 6.5$ Hz, *Me* 5), 0.80 (d, 3 H, $J = 7$ Hz, *Me* 2), 0.74 (s, 3 H, *Me*), 0.69 (s, 3 H, *Me*), irrad. at 3.49, 2.34, and 0.80 ppm did not show clear effects, irrad. at 1.38 (*Me* 5) produced a sharp s at 2.00 ppm (H 5).

15, synth. by *Jones*-oxidation of **14**; UV (*Et*OH): 321 (15 300), 290 (sh, 9 200), 251 (sh, 2 900), 240 (3 900), 215 (15 000), 204 (27 000); NMR ($CDCl_3$): 7.66 (d, 1 H, $J = 9.5$ Hz, umb. H 4), 7.41 (d, 1 H, $J = 9$ Hz, umb. H 5), 6.86 (dd, 1 H, $J = 9$ and ca. 2 Hz, umb. H 6), 6.83 (br. s, umb. H 8), 6.30 (d, 1 H, $J = 9.5$ Hz, umb. H 3), 3.85 (s, 2 H, $-CH_2OAr$), 2.87 (dd, 1 H, $J = 14$ and 5 Hz, H 3), 2.75 (q, 1 H, $J = 7$ Hz, H 5), 2.47–2.60 (m, 3 H), 2.25–2.40 (m, 2 H), 1.9–2.0 (m, 2 H), 1.23 (s, 3 H, *Me*), 1.17 (s, 3 H, *Me*), 1.14 (d, 3 H, $J = 7$ Hz, *Me*), 1.03 (d, 3 H, $J = 7$ Hz, *Me*), irrad. at 2.87 produced a broad signal of $w_{1/2}$ ca. 7 Hz at 2.50 ppm emerging from the group of 3 H at 2.47–2.60, irrad. at 1.03 (*Me* 2) did not show any clear effect; NMR (C_6D_6): 6.65 (d, 1 H, $J = 9$ Hz, umb. H 5), 6.62 (d, 1 H, $J = 9.5$ Hz, umb. H 4), 6.49 (br. d, 1 H, $J = 9$ Hz, umb. H 6), 6.47 (br. s, 1 H, umb. H 8), 5.91 (d, 1 H, $J = 9.5$ Hz, umb. H 3), 3.12 (s, 2 H, $-CH_2OAr$), 2.44–2.52 [m, 2 H, upon irrad. at 1.46 ppm this group resolves to a s at 2.47 (H 5, originally a q with $J = 7$ Hz) and a dd centered at 2.49 (H 3, $J = 14$ and 5 Hz)], 2.12–2.27 (m, 2 H), 2.02 (dd, 1 H, $J = 12$ and 3 Hz, H 8 a), 1.50–1.80 (m, 4 H), 1.46 (d, 3 H, $J = 7$ Hz, *Me* 5), 0.79 (s, 3 H, *Me*), 0.72 (d, 3 H, $J = 7$ Hz, *Me* 2), 0.63 (s, 3 H, *Me*), irrad. at 2.02 and 0.72 did not show clear effects, for irrad. at 1.46 see above for the region 2.44–2.52 ppm.

16, *karatavicinol*[37], 6 mg, $Rf = 0.17$; NMR ($CDCl_3$): 5.47 (br. t, 1 H, J ca. 6.5 Hz, H 2), 5.19 (br. t, 1 H, $w_{1/2} = 13$ Hz, H 6), 4.60 (d, 2 H, $J = 6.5$ Hz, $-CH_2OAr$), 3.35 (dd, 1 H, $J = 10$ and 2 Hz, H 10), 2.0–2.3 (m, 10 H), 1.77 (br. s, 3 H, olefin. *Me*), 1.63 (br. s, 3 H, olefin. *Me*), 1.21 (s, 3 H, *Me*), 1.16 (s, 3 H, *Me*).

17, *tadshikorin*[38], 6 mg, $Rf = 0.32$; NMR ($CDCl_3$): 5.58 (t, 1 H, $J = 7$ Hz, H 2), 5.45 (d, 1 H, $J = 9$ Hz, H 10), 5.08 (t, 1 H, $J = 7$ Hz, H 4), 5.00 (br. t, 1 H, $J = 6$ Hz, H 6), 4.63 (d, 2 H, $J = 7$ Hz, $-CH_2OAr$), 4.57 (m, 1 H, H 9), 2.2–2.4 (m, 4 H), 2.04 (s, 3 H, CO*Me*), 1.82 (s, 3 H, *Me*), 1.72 (s, 3 H, *Me*), 1.69 (s, 3 H, *Me*), 1.62 (s, 3 H, *Me*).

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