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A Novel Iridoid Glucoside Isolated from *Lamium album* L.

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Whole plants of white dead-nettle (*Lamium album* L., Labiatae) contain, as the major glucoside, a novel iridoid. Its structure *1* is assigned mainly on the basis of PMR-data for the glucoside itself, its acetates, and bis-benzylidene derivatives. The aglucone, set free by hydrolysis with emulsin, is characterized as a triacetate. Proton coupling constants are utilized for estimating the most favoured conformations of the individual compounds. The results are in accord with those expected from considerations of steric interactions.

The genus *Lamium* is rich in iridoid glucosides.[1,2] In the white dead-nettle, *L. album* L. we have found the major glucoside to be a novel iridoid for which we propose the name lamiridoside** (for data, see Tables 1 and 3).

The PMR-spectrum of lamiridoside (*1*, see Table 1) exhibits absorptions typical for iridoid glucosides possessing a C-4 methoxycarbonyl grouping. Signals at 7.53, 5.68, and 3.82 ppm can be ascribed to H-3, H-1, and $COOCH_3$, respectively.[2] The doublet character ($J = 0.8$ Hz) of the signal at 7.53 ppm signifies the presence of a proton at C-5, a novelty in so far as all formerly known iridoids from *Lamium* species carry a hydroxy group at C-5.[1] Irradiation at 7.53 and 5.68 ppm ($J = 1.5$ Hz) revealed absorptions attributable to the H-5 and H-9 protons at 2.97 ppm and 2.89 ppm, respectively. A signal at 4.10 ppm was assigned to H-6 since double resonance experiments showed it to couple with both H-5 ($J = 3$ Hz) and another proton absorbing at 3.72 ppm ($J = 4.5$ Hz), *viz.* H-7. The last signal arising from the non-sugar moiety, a three-proton singlet at 1.27 ppm, could be assigned to a methyl group positioned at a tertiary carbon carrying an

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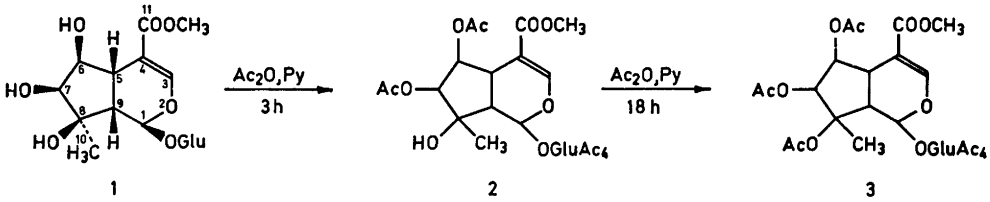
** See note, at the end of this paper.

Table 1. PMR-data[a].

Compound	δ-Values in ppm from internal TMS[b]								Coupling constants (Hz)[c]				
	H_1	H_3	H_5	H_6	H_7	H_9	CH_3-10	OCH_3	$J_{6,7}$	$J_{5,9}$	$J_{5,6}$	$J_{3,5}$	$J_{1,9}$
1	5.68	7.53	2.97	4.10	3.72	2.89	1.27	3.82	4.5	11	3	0.8	1.5
2	5.53	7.39	3.09	5.29	4.97	2.93	1.32	3.70	5	11	4	1.3	1.5
3	5.73	7.41	3.06	5.42	5.51	3.26	1.57	3.73	4.5	11	3.5	1.0	1.0
4	5.19	7.49	3.24	4.00	4.25	2.65	1.44	3.74	5	8	8	1	7.5
5	5.50	7.5	3.30	5.42	4.36	2.81	1.47	3.74	6	8.5	4	1.5	4
6	5.58	7.38	3.08	4.74	4.08	2.79	1.27	3.75	6	10	0.5	2	< 0.5
7	5.59	7.45	3.02	4.68	4.81	3.16	1.53	3.77	5.5	10	0.5	1.5	< 0.5
8	5.33	—	3.55	5.05	4.33	2.56	1.52	3.71	5.5	8	8	—	7.5
9	5.58	7.39	3.06	4.80	4.06	2.71	1.20	3.77	5	11	1	2	1
10	5.60	—	3.05	4.79	4.85	3.05	1.48	3.79	4.5	—	< 0.5	—	< 0.5
12	6.37	7.41	3.18	5.28	5.00	2.81	1.33	3.74	5	11	4	1.3	1.9

[a] The spectra were recorded on a Varian HA-100 instrument in $CDCl_3$, with TMS as an internal reference, except for *1*, recorded in D_2O, with DSS as a reference. [b] ± 0.02 ppm. [c] ± 0.5 Hz.



1 2 3

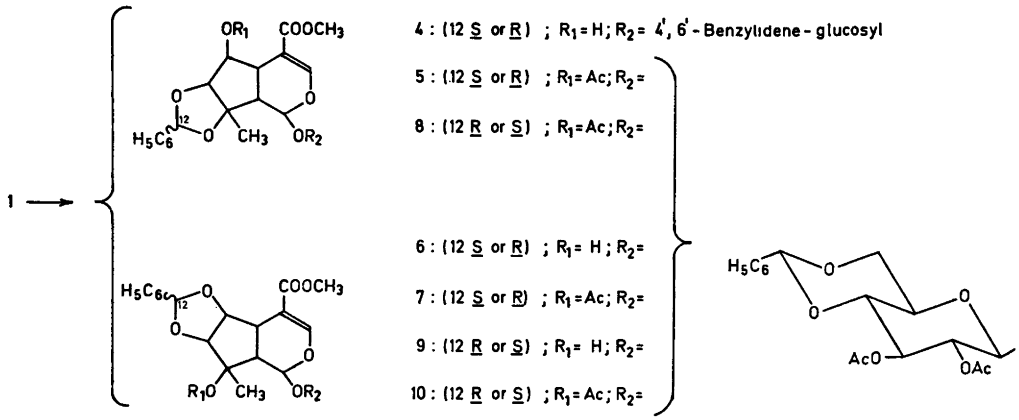
oxygen atom. Taken together, these data support the gross structure *1* (disregarding stereochemistry) for lamiridoside. In keeping herewith, acetylation afforded a hexaacetate *2* or a heptaacetate *3*, depending on conditions. The PMR-spectra of the acetates (Table 1) provided additional evidence for the proposed structure. Thus, acetylation of the tertiary hydroxyl group caused low field shifts of the absorptions of the neighbouring protons, the signals arising from H-7, H-9, and CH_3-10 being shifted 0.54, 0.33, and 0.25 ppm, respectively.

Assuming configurational similarity of lamiridoside with other iridoids,[2] H-1, H-5, and H-9 can be placed in α-, β-, and β-positions, respectively (*vide infra*), leaving the configurations at the three carbinol centers in the five-membered ring undecided. The coupling constants $J_{5,6}$ and $J_{6,7}$ of *1*, *2*, and *3* are of little help here, since they all fall within the range of 3 – 5 Hz, and hence are compatible with a *cis*- as well as a *trans*-junction.[4,5]

Other means were therefore sought to settle the stereochemistry. Treatment of *1* with benzaldehyde and zinc chloride yielded a mixture of bis-benzylidene derivatives. The PMR-spectrum of this mixture showed, within the region of the benzylic protons (5.5 – 6.5 ppm), a broad singlet attributable to the 4′,6′-benzylidene-glucosyl moiety and four different signals of varying intensity at lower field, signifying the presence of at least four isomers in the reaction mixture. From this mixture all four isomers were isolated either as such, or in acetylated forms.

Chromatography of the mixture afforded the amorphous compound *4*, converted upon acetylation under mild conditions into the crystalline triacetate *5*. A pronounced shift to low field (1.42 ppm) of the H-6 signal on passing from *4* to *5*, when compared to those of H-7 and CH_3-10 (0.11 and 0.03 ppm, respectively), securely positions the second benzylidene group at C-7 and C-8 in these compounds.

Acetylation under mild conditions of the remaining mixture afforded, after chromatography, a crystalline diacetate *6*. Acetylation of *6* under forcing conditions produced the triacetate *7*. On comparing the PMR-spectra of *6* and *7*, it appears that the low field shifts of H-7, H-9, and CH_3-10 (0.73, 0.37, and 0.26 ppm, respectively) are similar to those found by going from *2* to *3*. Consequently, *6* and *7* can be formulated as 6,7-benzylidene derivatives.



Additional to *6*, another crystalline compound could be isolated from the remaining mixture, namely the triacetate *8*, formulated as a 7,8-benzylidene compound mainly because of the low field position of H-6 (5.05 ppm), suggesting the presence of an acetoxy group at C-6.

The mother liquor from the crystallization of *8* was rich in the diacetate *9*, which was not obtained in the pure state (only a PMR-spectrum was recorded of this derivative). Acetylation of the latter, under forcing conditions, yielded the triacetate *10*. Comparison of the PMR-spectra of *9* and *10* revealed that H-7, H-9, and CH_3-10 were shifted 0.79, 0.34, and 0.28 ppm, respectively, towards lower field, shifts similar to those observed on going from *2* to *3*, and from *6* to *7*. Consequently, *9* and *10* must be 6,7-benzylidene compounds and hence epimers of *6* and *7*, respectively.

Since both 6,7- and 7,8-benzylidene compounds are formed in the reaction with benzaldehyde, it follows that all the hydroxy groups of the iridoid moiety in lamiridoside are positioned on the same face of the molecule.[3] The remaining problem, *viz.* on which side, is resolved by consideration of the coupling constants $J_{5,6}$ for the compounds *6*, *7*, *9* and *10*. The consistently low value of $J_{5,6}(\leq 1$ Hz) demands a dihedral angle close to 90° between H-5 and H-6, necessitating a *trans* relationship of these protons.[4,5] Consequently, the hydroxy groups at C-6, C-7, and C-8 in lamiridoside are all occupying β-positions.

Hydrolytic cleavage of *1* with emulsin afforded glucose, identified by paper chromatography with authentic glucose as a reference, and, in addition, the amorphous aglucone *11*, which was converted, under mild conditions, into a triacetate (*12*). By comparison of the PMR-spectra of *2* and *12*, the stereochemistry at C-1 in *12* appears to be identical with that of lamiridoside and its derivatives. The small value of $J_{1,9}$ (1.9 Hz) in *12* clearly places H-1 in an equatorial position, an arrangement prevailing also in the other derivatives, except in *4*, *5*, and *8*. In the latter, the overall conformation of the dihydropyrane ring is obviously altered, with H-1 assuming more or less an axial position, resulting in an increased value of the coupling constant $J_{1,9}$. This change in conformation is accompanied by low field shifts of H-5 and CH_3-10, and shifts to higher field of H-9. Assuming an α-situated acetoxy group at C-1 in *12*, an equatorial H-1 would require a conformation similar to that prevailing in *4*, *5*, and *8*; this is definitely not in accord with the observed PMR-data.

Turning to the glucose moiety of lamiridoside, the PMR-spectra of *1* and its derivatives clearly show the presence of a pyranose ring, attached to the aglucone through a β-glucosidic linkage, as evidenced by the large coupling constant $J_{1'2'}$ (7.5 Hz) observable in *1* and *4*.

In the above conclusions, the presence of a *cis*-fused ring system was assumed. Inspection of a Dreiding model shows the alternative *trans*-fused system to be far more strained, permitting only a single conformer for each of the two *trans*-fused forms. In both of these, the cyclopentane ring will adopt a twist form, namely $^5T_9$ for the 5β,9α- and $^9T_5$ for the 5α,9β-fusion.[6] These conformations demand dihedral angles between H-5 and H-6 of 170° or 20°, respectively, incompatible with the observed coupling constants ranging from 0.5 to 8 Hz. Moreover, the ring strain should be reflected in a shift of the UV-maximum when compared with that of the known *cis*-fused compounds, all absorbing within the 230 – 240 nm range.[2] Again, the compounds *1*, *2*, *3*, and *12* all exhibit UV-absorptions within the range 232 – 238 nm, in accord with the presence of *cis*-fused rings.

PMR has recently been shown to be of value in assessing the most favoured conformations of five-ring systems like furanosides.[6,7] Applying the treatment given by Hall *et al.*[6] for furanosides to the cyclopentane ring in the iridoid skeleton, we arrive at reasonable conclusions for lamiridoside and its derivatives. In the "cycle of pseudorotation" (*Cyclops*) of interchanging envelope (*V*) and twist (*T*) forms for this system,[6] we have substituted C-8, C-7, C-6, C-5, and C-9 with the corresponding atoms in the furanoses, *viz.* O, C-1, C-2, C-3, and C-4, respectively, and adopted the angle values measured by Hall *et al.* The error introduced by this approximation is considered to be negligible in the present approach.

The coupling constants listed in Table 1 can be used to divide the compounds into four groups as specified in Table 2 (*10* cannot be classified since $J_{5,9}$ is unknown because H-5 and H-9 have closely similar chemical shifts).

Table 2. Favoured conformers and data for estimation of these.

Group (compounds)	$J_{measured}$	Calculated dihedral angle ± 10°	Favoured conformers	Dihedral angle in favoured conformers
A (*1, 2, 3, 12*)	$J_{6,7}$ 4.5 – 5	30 – 55	^7V $^7T_8$	50
	$J_{5,6}$ 3 – 4	115 – 145		140 – 150
	$J_{5,9}$ 11	0 – 10		0 – 20
B (*4, 8*)	$J_{6,7}$ 5 – 5.5	25 – 50	V_6 $^7T_6$	50 – 60
	$J_{5,6}$ 8	150 – 170		170
	$J_{5,9}$ 8	10 – 30		20 – 30
C (*5*)	$J_{6,7}$ 6	20 – 45	V_8 $^7T_8$	30 – 50
	$J_{5,6}$ 4	120 – 145		120 – 140
	$J_{5,9}$ 8.5	10 – 30		20 – 30
D (*6, 7, 9*)	$J_{6,7}$ 5 – 6	25 – 50	V_7 $^6T_7$	50 – 60
	$J_{5,6}$ 0.5 – 1	65 – 120		70 – 90
	$J_{5,9}$ 10 – 11	0 – 10		0 – 20

Table 3. Optical rotations and elemental analyses of lamiridoside and derivatives.

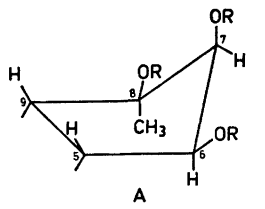
Compound	$[\alpha]_D^{21}$ (*c*, EtOH)	Formula	Analyses Calculated C	Calculated H	Found C	Found H
1	– 132(0.4)	$C_{17}H_{26}O_{12}$. $0.75H_2O$	46.85	6.36	46.83	6.33
					46.95	6.39[b]
2	– 107(0.6)	$C_{29}H_{38}O_{18}$	51.53	5.67	51.86	5.52
3	– 83(0.3)	$C_{31}H_{40}O_{19}$	51.96	5.63	51.82	5.72
4	– 104(0.3)	$C_{31}H_{34}O_{12}.H_2O$	60.39	5.89	60.67	5.81
					60.63	5.84[b]
5	– 142(0.1)	$C_{37}H_{40}O_{15}$	61.32	5.56	61.11	5.63
6	– 162(0.4)	$C_{35}H_{38}O_{14}$	61.57	5.61	61.40	5.68
7	– 122(0.9)	$C_{37}H_{40}O_{15}$	61.32	5.56	61.07	5.64
8	– 115(0.6)[a]	$C_{37}H_{40}O_{15}$	61.32	5.56	61.02	5.41
10	– 152(0.4)	$C_{37}H_{40}O_{15}$	61.32	5.56	61.51	5.71
11	– 108(0.2)	$C_{17}H_{22}O_{10}$	52.85	5.74	52.96	5.90

[a] In $CHCl_3$. [b] After additional drying.

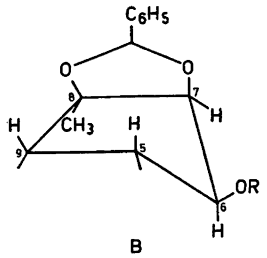
Using Karplus relationship * for calculating the dihedral angles and arbitrarily adding and subtracting 10° to the values found, a conservative estimate of the angles is obtained (se Table 2). Comparing the values with those derived from the *Cyclops* sequence and eliminating conformers which do not fit, first for $\angle H_6H_7$, then for $\angle H_5H_6$ and $\angle H_5H_9$, only a small number of conformers are left for each group of compounds (see Table 2).

* We have used the curve as given by Williams and Fleming.[8]

Thus, group A, comprising the compounds *1*, *2*, *3*, and *12*, is found preferentially to adopt the ^7V and $^7T_8$ conformations. Inspection of models of these conformers leaves only one possibility for the conformation of the dihydropyrane ring, namely a distorted half chair (HC_9^1) with an axial orientation of the glucose moiety and $\angle H_1H_9$ close to 70°. In the ^7V conformation (depicted as *A*) the interactions between the bulky groups are minimal, the oxygen substituents on C-6 and C-8 being pseudo-equatorial and that on C-7 together with the methyl group on C-8 pseudo-axial.



A



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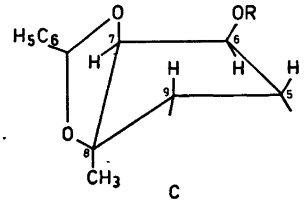
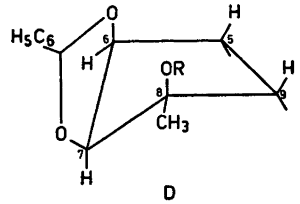


C



D

Group B, consisting of the 7,8-benzylidene compounds *4* and *8*, is found to favour the V_6 and ${}^7T_6$ conformers, of which V_6 is depicted as *B*. Again, this conformation introduces only minimal steric interactions of the bulky groups on the five-membered ring. The dihydropyrane ring in this case, however, is in an almost planar conformation, save for C-1 pointing downwards and giving rise to an equatorial position of the sugar moiety.

In group C, solely made up of *5* (the triacetate of *4*) the conformation of the molecule is less obvious. The above treatment leads to two sets of possible five-ring conformers, *viz.* ${}^8V$ and $V_8-{}^7T_8$. Models indicate, however, that the former requires an $\angle H_1H_9$ of either 180° (HC_9^1) or 90° ($Boat_{0,5}$), the latter agreeing with that calculated for *5*, namely 120 – 140°. Consequently, the ${}^8V$ conformation can be disregarded. The change observed in going from *4* to *5* is not easily explained, as a larger steric interaction prevails in $V_8-{}^7T_8$ (V_8 depicted as *C*). However, the effects of the benzylidene groups, with their unknown stereochemistry, are obscure.

Considering the last group of compounds, D, comprising the 6,7-benzylidene compounds *6*, *7*, and *9*, we find only one set of preferred conformers V_7 and ${}^6T_7$ for the cyclopentane ring (V_7 is depicted as *D*). The dihydropyrane ring in this case, as in group B, is almost planar except for C-1, here pointing upwards and giving rise to an axial position of the glucose moiety.

Obviously, the number of low-energy conformers of the five-ring is restricted through fusion with the dihydropyrane ring, which, on the other hand, is conformationally influenced by the presence of the five-membered ring. The present results indicate that in the mutual interactions between the two rings, the nature of the substituents in the five-ring play a dominant role.

However well the conformations arrived at by consideration of sterical interactions and analysis of coupling constants coincide, it is important to stress the element of speculation involved in the latter analyses, both in the present and previous work.[6,7] It is hoped, however, that considerations such as those described above may help in acquiring a more detailed picture of the actual state of iridoid molecules in solution.

EXPERIMENTAL

Melting points are uncorrected and were determined in capillary tubes in a heated bath. Preparative TLC was performed on 20 × 40 cm plates coated with 1 mm layers of silica gel PF_{254} (Merck); bands were detected by UV-light. Analyses were performed at Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany.

Isolation of lamiridoside (*1*). Fresh plant material * (850 g, collected close to the labora-

* A voucher has been deposited in the Botanical Museum of the University of Copenhagen under the file No. IOK 152/72.

tory) was homogenized in EtOH and worked up as previously described.[9] The resulting Me_2CO eluate (*ca.* 8 g) was chromatographed twice on SiO_2 (300 g), with $CHCl_3$-MeOH (3:1) as the eluent. On standing, the main fraction (3.2 g) deposited crystalline KNO_3 (400 mg, identified by the IR-spectrum).[10] Purification was achieved by adsorption on activated carbon (10 g), washing with H_2O, and elution of the glucoside fraction with MeOH. A colourless, amorphous product was obtained by evaporating the solvent (2.0 g; 0.24 %). λ_{max}(EtOH) 238 nm (ε 10 200). PMR: 4.83 ppm (*d*, $J_{1'2'} = 7.5$ Hz; H-1'), 3.35 – 3.95 ppm (absorptions corresponding to the sugar-protons in glucosides); further data in the tables.

Lamiridoside hexaacetate (2). Acetylation of *1* (490 mg), in pyridine (5 ml) and Ac_2O (3 ml) for 3 h at room temperature, gave, after chromatography on SiO_2 (Et_2O – EtOAc; 9:1), *2* (484 mg). Recrystallization from MeOH gave an analytical specimen, m.p. 126.5 – 128°. λ_{max}(EtOH) 234 nm (ε 10 650). Further data in the tables.

Lamiridoside heptaacetate (3) was obtained analogously, by prolonging the acetylation time to 18 h; m.p. 189 – 190°. λ_{max} (EtOH) 232 nm (ε 10 100). Further data in the tables.

Preparation of benzylidene derivatives. 1 (710 mg) was stirred with freshly distilled C_6H_5CHO (23 ml) and anhydrous $ZnCl_2$ (1.2 g) for 3 h at room temperature. The homogeneous, slightly yellow reaction mixture was poured into saturated $NaHCO_3$ solution (100 ml) and extracted with pentane (3 × 100 ml) which was then discarded. The aqueous solution was extracted with EtOAc (3 × 150 ml) which, after drying, was concentrated *in vacuo*. The residue (944 mg) was subjected to preparative TLC to give two bands by elution with $CHCl_3$ – EtOAc (1:1); a faster running band (*fract. A*, 490 mg) and a slower running band (*fract. B*, 165 mg). The latter was rechromatographed to give a homogeneous (PMR, TLC), amorphous product: *7,8 – 4',6'-dibenzylidene lamiridoside (4)*. (Elemental analyses showed this preparation to retain about 1 mol of H_2O, which could not be removed even by rechromatography followed by rigorous drying in high vacuum). PMR-spectrum: 7.30 – 7.60 ppm (*m*; 11 H, 10 arom. H and H-3); 6.20 and 5.44 ppm (*s*'s; 2 benzylidene H); 4.28 ppm (*d*; $J = 7.5$ Hz, H-1'). Further data in the tables.

Acetylation of *4* (Py/Ac_2O; 5 h, 25°) provided *6,2',3'-triacetyl 7,8 – 4',6'-dibenzylidene lamiridoside (5)*, which was crystallized from MeOH to give a colourless solid, m.p. 136 – 137°. PMR-spectrum: 7.30 – 7.60 ppm (*m*, 11 H, 10 arom. H and H-3); 6.03 and 5.52 ppm (*s*'s; 2 benzylidene H); *ca.* 5.4 ppm (*m*; H-3'); 5.02 ppm (*m*, H-1' and H-2'); 2.14, 2.05 and 1.95 ppm (3 × OAc). Further data in the tables.

Fraction A (see above) was acetylated (Py/Ac_2O; 5 h, 25°) and gave, after work up, a mixture (630 mg), which was separated into two bands (*fract. C* and *D*) by preparative TLC (C_6H_6 – Et_2O; 3:1). The slower running fraction *C* (126 mg) was recrystallized from MeOH to give *2',3'-diacetyl 6,7 – 4',6'-dibenzylidene lamiridoside (6)* as colourless crystals, m.p. 221 – 223° (softening and resolidifying at 141 – 145°). PMR-spectrum: 7.30 – 7.60 ppm (*m*; 10 arom. H and H-3); 5.79 and 5.49 ppm (*s*'s; 2 benzylidene H); 5.32 ppm (*m*; H-3'); 4.99 ppm (*m*; 2H, H-1' and H-2'); 4.37 ppm (*dd*; $J = 4$Hz and 10 Hz, H-4'); 2.02 and 1.90 ppm (2 × OAc). Further data in the tables.

Acetylation of *6* overnight at 80 – 90°, followed by preparative TLC (C_6H_6 – Et_2O; 1:1) gave the amorphous *8,2',3'-triacetyl 6,7 – 4',6'-dibenzylidene lamiridoside (7)*. PMR-spectrum: 7.30 – 7.60 ppm (*m*; 10 arom. H and H-3); 5.77 and 5.51 ppm (*s*'s; 2 benzylidene H); 5.33 ppm (*m*; H-3'); 5.01 ppm (*m*; H-1' and H-2'); 2.03, 2.01, and 1.91 ppm (3 × OAc). Further data in the tables.

From *fraction D* (465 mg) above a compound separated on crystallization from EtOH. Recrystallization gave *6,2',3'-triacetyl 12*-epi-*7,8 – 4',6'-dibenzylidene lamiridoside (8)* as colourless crystals (285 mg) m.p. 204°. PMR-spectrum: 7.30 – 7.60 ppm (*m*; 10 arom. H and H-3); 5.95 and 5.49 ppm (*s*'s; 2 benzylidene H); *ca.* 5.4 ppm (*m*; H-3'); 5.05 ppm (*m*; H-1' and H-2'); 4.40 ppm (*m*; H-4'); 2.03, 1.96 and 1.91 ppm (3 × OAc). Further data in the tables.

The mother liquors from the crystallization of *8* contained, according to PMR, *8* and another compound in the proportion 1:4. Repeated chromatography (Et_2O – EtOAc-pentane; 1:1:1) resulted in an improvement of the ratio to 1:10. This inhomogeneous preparation, mainly consisting of *2',3'-diacetyl 12*-epi-*6,7 – 4',6'-dibenzylidene lamiridoside (9)*, was not subjected to further purification; only a PMR-spectrum was recorded: 7.30 – 7.60 ppm (*m*; 10 arom. H and H-3); 6.25 and 5.51 ppm (*s*'s; 2 benzylidene H); 5.35 ppm (*m*; H-3'); 5.01 ppm (*m*; H-1' and H-2'); 4.42 ppm (*m*; H-4'); 2.04 and 1.92 ppm (2 × OAc). Further PMR-data in Table 1.

Acetylation of the preparation above (130 mg) for 3 days at 80° gave, after work-up and chromatographic separation (C_6H_6 – Et_2O; 1:1), *8,2',3'-triacetyl 12*-epi-*6,7-4',6'-dibenzylidene lamiridoside (10)* as a colourless foam. PMR-spectrum: 7.30 – 7.60 ppm (*m*; 10 arom. H and H-3); 6.14 and 5.56 ppm (*s*'s; 2 benzylidene H); 5.38 ppm; (*m*; H-3'); 5.04 ppm (*m*; H-1' and H-2'); 4.46 ppm (*dd*; $J = 4$ and 9.5 Hz, H-4'); 2.09, 2.07, and 1.95 Hz (3 × OAc). Further data in the tables.

Enzymic hydrolysis of lamiridoside. (1) (500 mg) was dissolved in H_2O (15 ml) and emulsin (200 mg) was added. After stirring for 3 h, *1* had disappeared (TLC), and the mixture was filtered through activated carbon (5 g) and celite (4 g). The filter cake was washed with H_2O (100 ml), and glucose was identified

in the filtrate by co-chromatography with authentic glucose on paper (solvent: BuOH-EtOH-H_2O; 4:1:4). Elution of the filter cake with MeOH (100 ml), and evaporation of the solvent gave an apparently stable, sirupy residue (196 mg), which could not be induced to crystallize. Its PMR-spectrum was in accordance with that expected for the aglucone. Without further purification, the aglucone was acetylated (Py/Ac_2O; 2 h, room temp.). Preparative TLC with $C_6H_6-Et_2O$ (2:1) as the eluent and extraction of the main band gave the *aglucone triacetate (11*, 70 mg). Crystallization from $EtOAc-Et_2O$ afforded the pure compound, m.p. 153–155°. λ_{max} (EtOH) 232 nm (ε 10 450). Further data in the tables.

Note added in proof. After the present paper was submitted, Brieskorn and Ahlborn[11] reported the isolation of the same glucoside, named 'lamalbid', from '*Flores lamii albi*'. We accept the latter name and hence consider the designation 'lamiridoside' as redundant.

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