Journal of Natural Products
Vol. 50, No. 6, pp. 1048-1054, Nov-Dec 1987

PHYTOCHEMICAL INVESTIGATIONS ON *PENSTEMON HIRSUTUS*

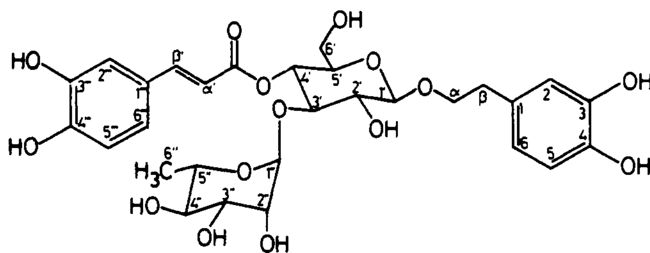
BIRGIT GERING* and MAX WICHTL

Institut für Pharmazeutische Biologie, Philipps-Universität Marburg, Deutschhausstrasse 17½, D-3550 Marburg, FRG

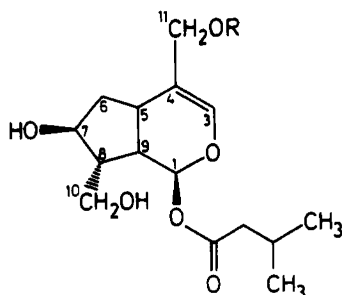
ABSTRACT.—Phytochemical investigations on *Penstemon hirsutus* resulted in the isolation of a phenylpropanoid glycoside, two iridoids, and two acyclic monoterpenes. Their structures have been elucidated by fdms, ^{1}H-nmr, and ^{13}C-nmr spectroscopy. The major compound **1**, a caffeic acid ester, is identical with acteoside (syn. verbascoside, kusaginin). The novel iridoid glycoside, patrinalloside [**2**] (patrinoside-aglucone-11-*O*-β-D-allopyranoside), and its aglycone, patrinoside-aglucone [**3**], have been isolated and identified. Besides the iridoid compounds, two additional monoterpenes of acyclic structure were isolated, 1-β-D-glucopyranosyl-8-hydroxy-3,7-dimethyl-2(*E*),6(*E*)-octadienoate [**4**] and 8-hydroxy-3,7-dimethyl-2(*E*),6(*E*)-octadienoic acid [**5**].

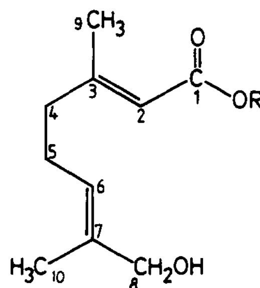
The occurrence of iridoid glycosides in several species within the genus *Penstemon* is well documented (1-5). Besides widely distributed compounds such as aucubin and catalpol, typical for the Scrophulariaceae, the presence of valeriana-type ester iridoids, e.g., penstemide, first reported by Jensen *et al.* (6) from *Penstemon deustus* Dougl., is remarkable. Moreover, McCoy and Stermitz (7) detected pyridine monoterpene alkaloids in flowers of *Penstemon whippleanus* A. Gray. Recently Junior isolated acetophenone glucosides from *P. whippleanus* (8) and *Penstemon pinifolius* Greene (9). In this report, we describe the isolation and structure elucidation of a phenylpropanoid glycoside from *Penstemon hirsutus* (L.) Willd., acteoside [**1**].

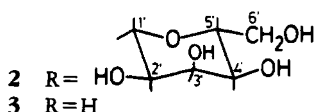
Acteoside was first isolated from the flowers of *Syringa vulgaris* L. (Oleaceae) (10), and its structure was assigned as 3,4-dihydroxy-β-phenylethoxy-*O*-α-L-rham-



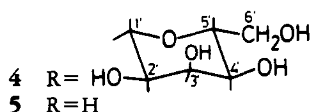
1







2 R=
3 R=H



4 R=
5 R=H

nopyranosyl-(1-3)-4-*O*-caffeoyl-β-D-glucopyranoside. Verbascoside (11-14) and kusaginin (15) are identical with acteoside (16-22), which exhibited antihypertensive and analgesic activities and potentiated antitremor L-dopa activity in animals (12).

The novel compound patrinalloside [**2**] is the major iridoid component of *P. hirsutus* leaves. The aglycone of **2**, patrinoside-aglucone [**3**], which was first reported from *Patrinia scabiosaefolia* Fischer (Valerianaceae) (23), has also been isolated from *P. hirsutus*. The compounds **4** and **5** are acyclic monoterpene derivatives of interesting structure with a view to the biosynthesis of iridoid glycosides. There are only a few reports of glycosides consisting of an acyclic monoterpene moiety occurring in species which are known to contain iridoids (24-26) or of acyclic monoterpene units linked to iridoids (1,27) or secoiridoids (28,29). The isolation procedure and the structure elucidation of all five compounds are presented in this paper.

RESULTS AND DISCUSSION

The viscous residue of a MeOH extract from dried, powdered leaves of *P. hirsutus* was separated from chlorophyll by continuous elution with $CHCl_3$ after column chromatography on Si gel. Separation of the extract by repeated cc and dccc yielded acteoside [**1**], patrinalloside [**2**], and compound **4**. A second MeOH extract from leaves of *P. hirsutus* was worked up in a different way. Removal of chlorophyll with $Pb(OAc)_2$ and separation of the extract by cc, subsequent dccc, and preparative tlc yielded patrinoside-aglucone [**3**] and compound **5**. The major compound **1** was detected by its uv fluorescence. After spraying with vanillin-H_2SO_4, it showed red spots that turned brown after heating. Acid-catalyzed hydrolysis (30) yielded L-rhamnose and D-glucose. The molecular formula $C_{29}H_{36}O_{15}$ was indicated by fdms, *m/z* 624 (100%, $[M]^+$) and 625 (48%, $[M+H]^+$). The ^{13}C-nmr spectrum proved the presence of caffeoyl, rhamnosyl, and glucosyl moieties plus a second aromatic part, 3,4-dihydroxyphenylethanol. All spectral data confirmed **1** to be identical with acteoside, which has been found in the Scrophulariaceae (13,19,21) before but is now reported for the first time from a species of the genus *Penstemon*.* Due to its structure, **1** is removed from extracts after work-up with $Pb(OAc)_2$, a procedure we often use for the separation of chlorophyll (5,31). Acteoside has also been isolated from *Penstemon richardsonii* Dougl. (31). Thus, the genus *Penstemon* is another example of the co-occurrence of iridoids and phenylpropanoid glycosides in certain species, which might be of chemotaxonomic value (32).

Patrinalloside [**2**] was obtained as a white, crystalline powder ($CHCl_3$/MeOH), mp 63°. On tlc it could be detected with vanillin-H_2SO_4 and heating as a purplish-brown spot. The ir spectrum of **2** exhibited signals typical for iridoid ester glycosides at 3400 (br, OH), 1740 (carbonyl), and 1660 cm^{-1} (enolether). The molecular formula $C_{21}H_{34}O_{11}$ was indicated by fdms, *m/z* 462 (26%, $[M]^+$). The ^{13}C-nmr spectrum of **2**, recorded in CD_3OD, indicated the presence of isovaleric acid linked at C-1 (93.59 ppm) of the iridoid skeleton and glycosidation at the hydroxyl function at C-11 (69.60 ppm).

The ^{13}C-nmr spectrum of **2**, recorded in D_2O, showed excellent agreement with the ^{13}C-nmr data recorded for patrinoside (33) regarding the iridoid skeleton. The chemical shifts of the sugar moiety of **2** agreed very well with the published ^{13}C-nmr data of β-D-allose in allosyldecaloside and epoxy-allosyldecaloside (34). The ^{13}C-^{1}H coupling constant of C-1′ (162.3 Hz) confirmed the β-configuration of the anomeric carbon (35). In a 2-D homonuclear ^{1}H-nmr spectrum (COSY) of compound **2** (400

*NOTE ADDED IN PROOF: In the meantime, acteoside was isolated from *Penstemon rosseus*: A. Lira-Rocha, R. Diaz, and M. Jimenez, *J. Nat. Prod.*, **50**, 331 (1987).

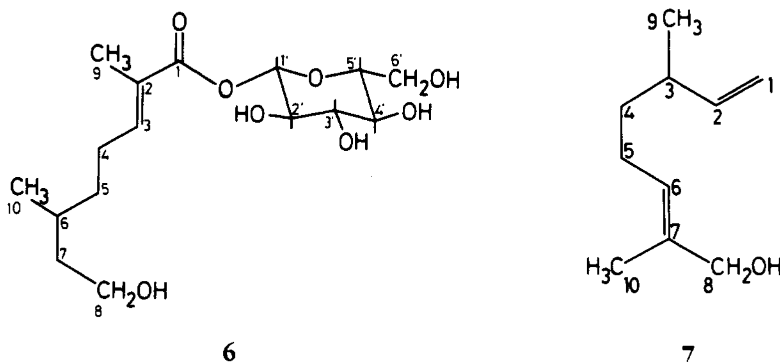
MHz, CD_3OD) all signals could be assigned. The ^{1}H-nmr spectrum of **2**, recorded in D_2O, showed very good agreement of the signals for H-1′ to H-6′ with the reported ^{1}H-nmr data of β-D-allose (36). The structure of patrinalloside [**2**] as patrinoside-aglucone-11-*O*-β-D-allopyranoside was confirmed by all experimental data.

Compound **3** belonged to the apolar fraction of the MeOH extract of *P. hirsutus*. A first hint concerning the structure of **3** was obtained from its color after detection with vanillin-H_2SO_4 and heating on tlc, which corresponded very well to patrinalloside [**2**]. The molecular formula $C_{15}H_{24}O_6$ was suggested by signals at *m/z* 300 (100%, $[M]^+$) and 301 (38%, $[M+H]^+$) in the fdms. The ^{13}C-nmr spectrum of **3**, recorded in CD_3OD, exhibited 14 signals (the signal of C-8 was overlapped by solvent peaks); five of them could be assigned easily to isovaleric acid attached to C-1 (93.43 ppm). By comparing the ^{13}C-nmr data of **2** and **3**, the latter can be identified as patrinoside-aglucone, which was first isolated from *Patrinia scabiosaefolia* Fischer (Valerianaceae) (23). The ^{1}H-nmr spectrum of **3** also confirmed its structure to be patrinoside-aglucone. Patrinoside and patrinoside-aglucone have also been isolated from *Viburnum* species (Caprifoliaceae) (33).

Compound **4** was isolated by dccc at a longer retention time than for **2**. On tlc **4** attracted attention because of a rapid change in color from bright blue to green within 1 h, after detection with vanillin-H_2SO_4 and heating. In the fdms of **4** the signal at *m/z* 386 (63%, $[M+K+H]^+$) indicated the molecular formula $C_{16}H_{26}O_8$. Enzymatic cleavage (30) with β-glucosidase in addition to acid-catalyzed hydrolysis (30) on tlc provided further information concerning the structure of **4** as a β-D-glucoside. The ^{13}C-nmr spectrum of **4** confirmed the presence of D-glucose. The signal of C-1′ at 95.22 ppm is shifted upfield (8 ppm) similarly to the anomeric carbon of β-D-glucose in **6** (26) (see Table 1) demonstrating the glycosidic linkage at the carboxyl function (C-1, 166.51 ppm). The absorptions at 116.05 ppm (C-2) and 163.85 ppm (C-3) resulted from a double bond in conjugation with the carboxyl function. The configuration, 2(*E*), and the substitution pattern could be assigned in relation to the ^{13}C-nmr data published for methylgeranoate and methylneroate (37) (see Table 1).

TABLE 1. ^{13}C-nmr Spectral Data of **6** (26), **7** (39), **4** (in CD_3OD, 100 MHz, δ ppm), Methylgeranoate, and Methylneroate (37)

Carbon atom	Compounds				
	6	**7**	**4**	methyl-geranoate	methyl-neroate
1	168.20	112.8	166.51	167.0	166.5
2	128.16	144.5	116.05	115.4	115.9
3	145.85	37.5	163.85	159.7	160.3
4	27.40	36.5	41.57	41.0	33.5
5	36.93	25.4	26.57	26.2	26.9
6	30.57	125.8	124.85	123.2	123.8
7	40.66	134.8	137.14	132.3	132.0
8	61.03	68.3	68.64	25.6	25.6
9	12.55	20.2	19.21	18.7	25.3
10	19.91	13.6	13.71	17.6	17.6
1′	95.94		95.22		
2′	74.05		73.96		
3′	78.12		78.69		
4′	71.10		71.15		
5′	78.77		78.06		
6′	62.40		62.40		
-OCH_3				50.5	50.6



6 7

Compound **4** must derive its structure from geranic acid as the chemical shifts of C-1 to C-5 express. The signals at 124.85 ppm (C-6) and 137.14 ppm (C-7) arose from a second double bond. The resonance at 68.64 ppm resulted from a vinylic hydroxymethyl group (C-8). Its value confirmed the *trans*-configuration, 6(*E*), at this center (*cis*-configuration gives rise to a signal at 60.5 ppm) and the position of the second methyl group at C-7 (38). The assignment of the signals of the carbons 7,8, and 10 (13.71 ppm) is in good agreement with the reported ^{13}C-nmr data for 8-hydroxy-3,7-dimethyl-1,6-octadiene [**7**] (see Table 1) (39). The ^{1}H-nmr spectrum of **4** showed the signals of two olefinic protons at 5.75 ppm (H-2) and 5.38 ppm (H-6). The resonances at 2.18 and 1.65 ppm referred to the vinylic methyl groups, 3H-9 and 3H-10, respectively. The absorptions at 2.26 ppm related to allylic-type protons (2H-4 and 2H-5). The structure of **4** as 1-β-D-glucopyranosyl-8-hydroxy-3,7-dimethyl-2(*E*),6(*E*)-octadienoate was confirmed by all spectral data. This substance has been isolated for the first time from a species of the genus *Penstemon*. Acyclic monoterpene moieties linked to iridoids were found in *Tecoma chrysantha* Jaqu., Bignoniaceae (27) (amareloside), *Penstemon nemorosus* Trautv., Scrophulariaceae (1) (nemoroside, nemorososide), and linked to secoiridoids in *Menyanthes trifoliata* L., Menyanthaceae (28,29) (foliamenthin, dihydrofoliamenthin, menthiafolin).

Compound **6** (1-β-D-glucopyranosyl-8-hydroxy-2,6-dimethyl-2-octaenoate) (26) from *Sambucus ebulus* L., Caprifoliaceae (Sambucaceae), represents a monoterpene glucoside similar to **4**. Bitter monoterpene glycosides have been encountered in *Viburnum phlebotrichum* (24) (phlebotricoside) and *Viburnum urceolatum* (25) (urceolide), Caprifoliaceae. In all cases the monoterpene moiety showed 2,6-dimethyl substitution whereas **4** has 3,7-dimethyl substitution.

Compound **5**, another apolar component of the MeOH extract of *P. hirsutus*, showed the same change in color after detection on tlc as **4**. Also, the Rf values of **5** were identical to those of the aglucone of **4**, obtained after enzymatic cleavage. Consequently, **5** must be 8-hydroxy-3,7-dimethyl-2(*E*),6(*E*)-octadienoic acid. The molecular formula $C_{10}H_{16}O_3$ was indicated by signals at 184 (42%, $[M]^+$) and 185 (78%, $[M+H]^+$) in the fdms. The ^{1}H-nmr spectrum of **5** is in very good agreement with the ^{1}H-nmr data recorded from **4** and proves the identity of **5** with the aglucone of the latter. Compound **5** is another rare monoterpene detected in a *Penstemon* species for the first time.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—*Penstemon hirsutus* was grown from seeds supplied by the Botanical Gardens Göttingen and Brüssel, and its identity was then confirmed (40). Voucher specimens have been deposited at the Institut für Pharmazeutische Biologie, Philipps-Universität Marburg, FRG.

Si gel 60 (70-230 mesh, Merck) was used for column chromatography (cc), and Si gel 60 F_{254} (Merck) prepared plates were used for tlc. Spots were detected by uv fluorescence and spraying with vanillin-H_2SO_4

followed by heating at 120° for 2-3 min. Dccc was carried out using a model DCC-A (Tokyo Rikakikai, Tokyo, Japan) and a Büchi B-670 DCC-Chromatograph. Ir spectra were recorded with a Perkin-Elmer 700 instrument in KBr pellets. Fdms were determined on a Varian-Mat 711 model. ^{1}H- and ^{13}C-nmr spectra were recorded at 400/100 MHz using Bruker WH 400 and JEOL GX 400 spectrometers.

ISOLATION PROCEDURE.—*Extract I*.—Dried, powdered leaves (38.2 g) were refluxed twice with 300 ml MeOH for 30 min. Concentration of the combined extracts in vacuo to near dryness furnished a viscous residue which was subjected to cc on Si gel (80 g). Before fractionation started, chlorophyll was separated by elution with $CHCl_3$ (3 liters). Then chromatography with $CHCl_3$-MeOH (99:1 to 80:20) afforded 450×20-ml fractions.

Isolation of **1**.—The residue of the polar fractions 341-431 (3 g) was chromatographed on Si gel (30 g) with EtOAc (4 liters) as eluent and afforded 66×60-ml fractions. After concentration of the combined fractions no. 9-18 in vacuo, 426 mg of **1** were obtained as a yellowish, amorphous powder; $C_{29}H_{36}O_{15}$ requires 624, fdms *m/z* 624 (100%, $[M]^+$), 625 (48%, $[M+H]^+$); ir (KBr) 3400 (br, OH), 1700 (C=O), 1635 (C=C), 1610, 1520 (arom. ring) cm^{-1}; ^{13}C nmr (100 MHz, CD_3OD) δ 168.28 (C=O), 149.77 (C-4‴), 147.99 (C-β′), 146.79 (C-3‴), 146.09 (C-4), 144.63 (C-3), 131.44 (C-1), 127.63 (C-1‴), 123.21 (C-6‴), 121.25 (C-6), 117.09 (C-5), 116.49 (C-2), 116.29 (C-2‴), 115.20 (C-α′), 114.66 (C-5‴), 104.16 (C-1′), 103.01 (C-1″), 81.63 (C-3′), 76.17 (C-2′), 75.98 (C-5′), 73.76 (C-4″), 72.32 (C-2″), 72.24 (C-α), 72.02 (C-3″), 70.55 (C-4′), 70.39 (C-5″), 62.33 (C-6′), 36.54 (C-β), 18.44 (C-6″); ^{1}H nmr (400 MHz, CD_3OD) δ 7.58 (d, *J*=15.9 Hz, H-β′), 7.04 (d, *J*=2.0 Hz, H-2‴), 6.95 (dd, *J*=8.1, 2.0 Hz, H-6‴), 6.77 (d, *J*=8.1 Hz, H-5‴), 6.69 (d, *J*=2.0 Hz, H-2), 6.66 (d, *J*=8.0 Hz, H-5), 6.55 (dd, *J*=8.0, 2.0 Hz, H-6), 6.26 (d, *J*=15.9 Hz, H-α′), 5.18 (d, *J*=1.6 Hz, H-1″), 4.37 (d, *J*=7.9 Hz, H-1′), 4.03 (m, H-α), 3.90 (dd, *J*=1.7, 3.2 Hz, H-2″), 3.80 (t, *J*=9.2 Hz, H-4″), 3.72 (m, H-5″), 3.57 (dd, *J*=3.2, 9.4 Hz, H-3″), 3.38 (dd, *J*=7.9, 9.2 Hz, H-2′), 2.78 (bt, H-β), 1.08 (d, *J*=6.2 Hz, H-6″).

Isolation of **2**.—After concentration of the combined fractions no. 278-340 (cc) in vacuo, the residue (1.5 g) was subjected to dccc [$CHCl_3$-MeOH-H_2O (5:6:4), descending flow] which furnished 192×12-ml fractions. Fractions no. 89-100 yielded 380 mg of **2**, which resulted as a white, crystalline powder from $CHCl_3$-MeOH (1:1), mp 63°; $C_{21}H_{34}O_{11}$ requires 462, fdms *m/z* 462 (26%, $[M]^+$); ir (KBr), 3400 (br, OH), 1740 (C=O), 1660 (enolether) cm^{-1}; $[\alpha]^{20}$D−69° (*c*=0.64, MeOH); ^{13}C nmr (100 MHz, CD_3OD) δ 173.35 (C=O), 139.92 (C-3), 116.58 (C-4), 101.02 (C-1′), 93.59 (C-1), 75.42 (C-5′), 73.44 (C-7), 72.96 (C-3′), 72.37 (C-2′), 69.60 (C-11), 69.05 (C-4′), 63.22 (C-6′), 62.27 (C-10), 44.17 (-CH_2-), 42.70 (C-9), 40.91 (C-6), 34.05 (C-5), 26.75 (-CH<), 22.62 (-CH_3, 2×); ^{13}C nmr (100 MHz, D_2O) δ 175.84 (C=O), 139.60 (C-3), 116.11 (C-4), 99.99 (C-1′), 93.53 (C-1), 74.37 (C-5′), 72.62 (C-7), 72.04 (C-3′), 71.15 (C-2′), 69.71 (C-11), 67.70 (C-4′), 62.03 (C-6′), 61.29 (C-10), 47.91 (C-8), 43.76 (-CH_2-), 41.73 (C-9), 39.65 (C-6), 32.98 (C-5), 26.27 (-CH<), 22.34 (-CH_3, 2×); ^{1}H nmr (400 MHz, CD_3OD) δ 6.36 (s, H-3), 5.90 (d, *J*=5.3 Hz, H-1), 4.63 (d, *J*=8.0 Hz, H-1′), 4.32 (m, H-7), 4.15 (AB center, *J*=11.6 Hz, 2H-11), 4.04 (t, *J*=3.0 Hz, H-3′), 3.84 (dd, ABX, *J*=1.7, 11.0 Hz, H-6′), 3.81 (dd, *J*=7.4, 11.0 Hz, 1H-10), 3.72 (dd, AB*X*, *J*=5.6, 10.9 Hz, H-6′), 3.47 (dd, *J*=3.0, 9.4 Hz, H-4′), 3.01 (m, H-5), 2.23 (-CH_2-), 2.18 (dt, *J*=5.3, 8.6 Hz, H-9), 2.03-2.09 (m, 2H, H-6, -CH<), 1.95 (m, H-8), 1.83 (m, H-6), 0.96 (d, *J*=6.6 Hz, -CH_3, 2×); ^{1}H nmr (400 MHz, D_2O) δ 6.45 (s, H-3), 5.94 (d, *J*=5.2 Hz, H-1), 4.72 (d, *J*=8.2 Hz, H-1′), 4.39 (m, H-7), 4.24 (AB center, *J*=11.9 Hz, 2H-11), 4.17 (t, *J*=3.0 Hz, H-3′), 3.90 (dd, ABX, *J*=1.7, 11.9 Hz, H-6′), 3.84 (dd, *J*=8.0, 11.1 Hz, 1H-10), 3.70 (dd, AB*X*, *J*=5.8, 11.9 Hz, H-6′), 3.62 (dd, *J*=3.0, 10.0 Hz, H-4′), 3.46 (dd, *J*=3.0, 8.2 Hz, H-2′), 3.03 (m, H-5), 2.34 (-CH_2-), 2.25 (dt, *J*=5.2, 8.7 Hz, H-9), 2.05-2.12 (m, 3H, H-8, H-6, -CH<), 1.89 (m, H-6), 0.96 (d, *J*=6.7 Hz, -CH_3, 2×).

Isolation of **4**.—After concentration of the combined fractions no. 144-155 (dccc) in vacuo, 67 mg of **4**, a very hygroscopic and unstable white substance, were obtained. $C_{16}H_{26}O_8$ requires 346, fdms *m/z* 386 (63%, $[M+K+H]^+$); ir (KBr) 3400 (br, OH), 1725 (C=O), 1645 cm^{-1}; $[\alpha]^{20}$D−14° (*c*=0.3; MeOH); ^{13}C nmr (100 MHz, CD_3OD) see Table 1; ^{1}H nmr (400 MHz, CD_3OD) δ 5.75 (s, H-2), 5.48 (d, *J*=7.9 Hz, H-1′), 5.38 (bt, H-6), 3.91 (bs, 2H-8), 3.83 (dd, ABX, *J*=2.0, 12.1 Hz, H-6′), 3.67 (dd, AB*X*, *J*=4.8, 12.1 Hz, H-6′), 2.26 (m, 4H, 2H-4, 2H-5), 2.18 (d, *J*=1.3 Hz, 3H-9), 1.65 (bs, 3H-10).

Extract II.—In two portions dried, powdered leaves of *P. hirsutus* (49.5 g and 46.6 g) were refluxed twice each with MeOH (300 ml and 200 ml) for 30 min. After filtration and concentration of the extracts in vacuo, the two residues were dissolved in 190 ml MeOH-H_2O (1:1) each. Chlorophyll was separated by addition of $Pb(OAc)_2$, and surplus lead was removed with Na_2HPO_4. After centrifugation, the iridoids and related compounds were extracted with $CHCl_3$-iPrOH (3:2) (3×200 ml) in both cases. The combined residues, 3.31 g and 2.7 g, were chromatographed on Si gel (160 g) with $CHCl_3$-MeOH (98:2 to 50:50) affording 134×160-ml fractions. Subsequent separation of the fractions no. 4-76 and 129-134 (1.2 g) by dccc with $CHCl_3$-MeOH-H_2O-iPrOH (50:60:40:1) resulted in 240×12-ml fractions.

Isolation of **3**.—Preparative tlc of the fractions no. 23-33 (92 mg) in Me_2CO-EtOAc-H_2O (40:56:4) yielded 28 mg of **3**, a white, amorphous powder (mp 92-95°); $C_{15}H_{24}O_6$ requires 300, fdms *m/z* 300 (100%, $[M]^+$), 301 (38%, $[M+H]^+$); $[\alpha]^{20}D-64°$ (c=0.3, MeOH); ^{13}C nmr (100 MHz, CD_3OD) δ 173.37 (C=O), 138.31 (C-3), 119.58 (C-4), 93.43 (C-1), 73.33 (C-7), 62.22 (C-10, C-11), 44.16 (-CH_2-), 42.84 (C-9), 40.77 (C-6), 33.18 (C-5), 26.79 (-CH<), 22.63 (-CH_3, 2×); ^1H nmr (400 MHz, CD_3OD) δ 6.27 (s, H-3), 5.93 (d, J=4.8 Hz, H-1), 4.30 (m, H-7), 3.97 (AB center, J=12.5 Hz, 2H-11), 3.81 (dd, J=7.2, 10.9 Hz, H-10), 3.72 (dd, J=5.7, 10.8 Hz, H-10), 2.97 (m, H-5), 2.20-2.24 (m, H-9), 2.23 (-CH_2-), 2.00-2.09 (m, H-6), 2.06 (-CH<), 1.95 (m, H-8), 1.79 (m, H-6), 0.96 (d, J=6.6 Hz, -CH_3, 2×).

Isolation of **5**.—Preparative tlc of the fractions no. 18-22 (36 mg) yielded 6 mg of **5** (yellow, amorphous substance); $C_{10}H_{16}O_3$ requires 184, fdms *m/z* 184 (42%, $[M]^+$), 185 (78%, $[M+H]^+$); ^{13}H nmr (400 MHz, CD_3OD) δ 5.66 (s, H-2), 5.38 (bt, H-6), 3.91 (s, 2H-8), 2.20 (m, 4H, 2H-4, 2H-5), 2.10 (d, J=1.3 Hz, 3H-9), 1.65 (bs, 3H-10).

ACKNOWLEDGMENTS

We thank PD Dr. St. Berger, FB Chemie, and Dr. Th. Kämpchen, FB Pharmazie, Universität Marburg, for recording the nmr spectra. We are indebted to Dr. K. Steinbach, FB Chemie, Universität Marburg, for the fdms. Financial support by the Fonds der Chemischen Industrie, Frankfurt, is gratefully acknowledged.

LITERATURE CITED

1. P. Junior, Habilitationsschrift, Marburg (1983).
2. P. Junior, *Planta Med.*, **50**, 530 (1984).
3. P. Junior, *Planta Med.*, 229 (1985).
4. R.K. Chaudhuri, O. Salama, and O. Sticher, *Tetrahedron Lett.*, **22**, 4061 (1981).
5. B. Gering, P. Junior, and M. Wichtl, *Phytochemistry*, **26**, 753 (1987).
6. S.R. Jensen, B.J. Nielsen, C.B. Mikkelsen, J.J. Hoffmann, S.D. Jolad, and J.R. Cole, *Tetrahedron Lett.*, 3261 (1979).
7. J.W. McCoy and F.R. Stermitz, *J. Nat. Prod.*, **46**, 902 (1983).
8. P. Junior, *Planta Med.*, **50**, 444 (1984).
9. P. Junior, *Planta Med.*, 218 (1986).
10. L. Birkofer, C. Kaiser, and U. Thomas, *Z. Naturforsch.*, **23b**, 1051 (1968).
11. M.L. Scarpati and F. Delle Monache, *Ann. Chim. (Rome)*, **53**, 356 (1963).
12. C. Andary, R. Wylde, R. Lafitte, G. Privat, and F. Winternitz, *Phytochemistry*, **21**, 1123 (1982).
13. G. Schilling, M. Hügel, and W. Mayer, *Z. Naturforsch.*, **37b**, 1633 (1982).
14. R. Hänsel and S. Kallmann, *Arch. Pharm. (Weinheim)*, **319**, 227 (1986).
15. A. Sakurai and T. Kato, *Bull. Chem. Soc. Jpn.*, **56**, 1573 (1983).
16. G. Nonaka and I. Nishioka, *Phytochemistry*, **16**, 1265 (1977).
17. H. Sasaki, H. Taguchi, T. Endo, I. Yosioka, K. Higashiyama, and H. Otomasu, *Chem. Pharm. Bull.*, **26**, 2111 (1978).
18. R. Cooper, P.H. Salomon, I. Kubo, K. Nakanishi, J.N. Shoolery, and J.L. Occolowitz, *J. Am. Chem. Soc.*, **102**, 7953 (1980).
19. O. Sticher and M.F. Lahloub, *Planta Med.*, **46**, 145 (1982).
20. B.E. Ellis, *Phytochemistry*, **22**, 1941 (1983).
21. Y. Shoyama, M. Matsumoto, and I. Nishioka, *Phytochemistry*, **25**, 1633 (1986).
22. H. Inouye, K. Inouye, T. Nichioka, and M. Kaniwa, *Phytochemistry*, **14**, 2029 (1975).
23. H. Taguchi and T. Endo, *Chem. Pharm. Bull.*, **22**, 1935 (1974).
24. T. Hase, T. Iwagawa, and K. Munesada, *Phytochemistry*, **21**, 1435 (1982).
25. T. Iwagawa and T. Hase, *Phytochemistry*, **22**, 255 (1983).
26. G.A. Gross, *Helv. Chim. Acta*, **70**, 91 (1987).
27. A. Bianco, P. Passacantilli, M. Nicoletti, and R. Alves de Lima, *Planta Med.*, **46**, 33 (1982).
28. P. Loew, Ch. v. Szczepanski, C.J. Coscia, and D. Arigoni, *Chem. Commun.*, 1276 (1968).
29. A.R. Battersby, A.R. Burnett, G.D. Knowles, and P.G. Parsons, *Chem. Commun.*, 1277 (1968).
30. D. Krüger and M. Wichtl, *Dtsch. Apoth. Ztg.*, **125**, 55 (1985).
31. B. Gering, Ph.D. Thesis, Marburg, West Germany: Philipps-Universität Marburg, 1987.
32. J.B. Harborne, *Z. Naturforsch.*, **21b**, 604 (1966).
33. V. Norn, Ph.D. Thesis, Lyngby, Denmark: Technical University of Denmark, 1978.
34. S.R. Jensen, C.B. Mikkelsen, and B.J. Nielsen, *Phytochemistry*, **20**, 71 (1981).
35. K. Bock and Ch. Pedersen, *J. Chem. Soc., Perkin Trans., 2*, 293 (1974).
36. A. De Bruyn, M. Anteunis, and J. van Belumen, *Bull. Soc. Chim. Belg.*, **86**, 259 (1977).

37. L. Crombie, R.W. King, and D.A. Whiting, *J. Chem. Soc., Perkin Trans., 1*, 913 (1975).
38. J.B. Stothers, "Carbon-13 nmr Spectroscopy," Academic Press, New York and London, 1972.
39. F. Bohlmann, R. Zeisberg, and E. Klein, *Org. Magn. Reson.*, **7**, 426 (1975).
40. H.A. Gleason in: "The New Britton and Brown: Illustrated Flora of the Northeastern United States and Adjacent Canada," Vol. 3, Hafner Publishing Company, New York and London, 1963.

Received 23 March 1987