Pergamon
0031-9422(94)00727-6
Phytochemistry, Vol. 38, No. 4, pp. 997 1001, 1995

0031 9422/95 $9.50 + 0.00

PHENYLPROPANOID ESTERS FROM *LAMIUM ALBUM* FLOWERS

JAROMIR BUDZIANOWSKI and LUTOSŁAWA SKRZYPCZAK

Department of Pharmaceutical Botany, K. Marcinkowski Academy of Medicine, Wieniawskiego 1, 61-712 Poznań, Poland

(*Received in revised form* 25 *August* 1994)

Key Word Index—*Lamium album*; Lamiaceae; flowers; phenylpropanoid glycosides; acylated flavonoids; lamalboside; 2^R-galactosylacteoside; *trans*- and *cis*-tiliroside; *trans/cis* isomers.

Abstract—Two phenylpropanoid glycosides, a new one, lamalboside (2^R-galactosylacteoside) and the known acteoside, the flavonol *p*-coumaroylglucoside, tiliroside, 5-caffeoylquinic acid (chlorogenic acid), along with rutoside and quercetin and kaempferol 3-*O*-glucosides were isolated from the flowers of *Lamium album*. Esters of glycosides were obtained as mixtures of *trans/cis* isomers. The presence of flavonoid *p*-coumaroylglucosides links *Lamium* to other members of the subfamily Lamioideae.

INTRODUCTION

Lamium album is a medicinal plant [1, 2] and previous chemical investigations showed the presence of flavonoids [3–5], iridoid glucosides [6, 7], phenolic and fatty acids [8–10], polysaccharides [11], triterpene saponins [12], stachydrin [10], amines, essential oil, condensed tannins and a mucilage [4].

The aim of the present work was isolation and identification of phenolics present in the flowers of *Lamium album*, which, after 2D TLC analysis, seemed to be not reported so far from this species. This paper describes the detection of *trans*- and *cis*-tiliroside (**1** and **2**), rutoside (**5**), acteoside (*trans*- and *cis*) (**7**), the unique 2^R-galactosylacteoside (lamalboside) (**8**) and previously suggested chlorogenic acid (**6**) [8] and quercetin and kaempferol 3-*O*-glucosides (**3**, **4**) [4].

RESULTS AND DISCUSSION

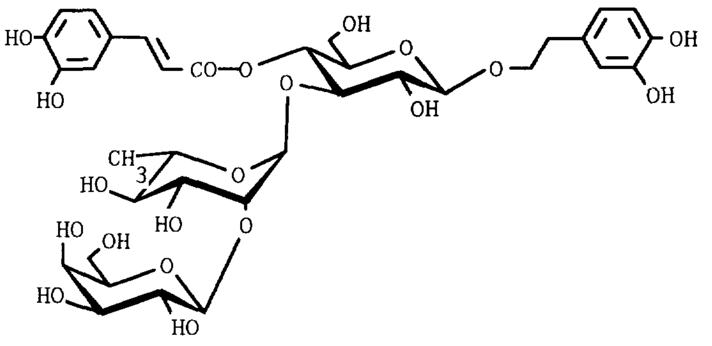
Separation of the water-soluble portion of the methanolic extract from the flowers by preparative TLC on cellulose and polyamide yielded **1**–**8**.

Compounds **3**–**6** were identified as quercetin 3-*O*-glucoside, kaempferol 3-*O*-glucoside, rutoside and chlorogenic acid, respectively, by direct comparisons with authentic samples and reported data [13–16].

Mixtures of **1** and **2** could not be separated by preparative TLC into individual components as they were very easily interconvertible. ^{1}H NMR (in CD_3OD) showed signals of tiliroside (kaempferol 3-*O*-(6‴-*O*-*trans*-*p*-coumaroyl)-glucopyranoside) (= **1**) [17] together with an additional weaker series of signals with a similar coupling pattern, except for those of the olefinic protons whose $J = 13$ Hz indicated a *cis*-configuration for the *p*-coumaroyl moiety [18]. Hence, the minor component, **2**, is identified as *cis*-tiliroside. Although both **1** and **2** were easily recognizable in the crude extract by 2D-TLC on cellulose in BAW (one spot) and 15% HOAc (two spots), the *cis*-isomer (**2**) was preferentially formed during chromatography. This assumption arose from the observation that the sample of unknown flavonoid obtained by column chromatography in previous work [5], which appeared now to be pure *trans*-tiliroside (= **1**) by its ^{1}H and ^{13}C NMR spectra [17, 19], showed two spots on 2D-TLC, like the mixture of **1** and **2**. This behaviour was quite similar to that of chlorogenic acid (= **6**) or *p*-coumaric acid itself [20].

Compound **7** was *trans*-acteoside (= *trans*-verbascoside) with a small admixture of *cis*-acteoside (ratio 6:1) from its ^{1}H and ^{13}C NMR spectra in accordance with the published data [21]. However, in contrast to data recorded for both isomers as separate compounds [21], we noticed no differences for resonances of the aglycone part (see Experimental). Our results may be more reliable since they were measured for isomers in a mixture, i.e. under the same conditions. The existence of the phenethyl part as a minor component was confirmed by ^{1}H NMR, which indicated that the quantitative ratio of the aglycone part to each of the caffeoyl, glucosyl and rhamnosyl moieties (each from both isomers as a sum) to be 1:1.

Compound **8** gave caffeic acid, glucose, rhamnose and galactose upon complete hydrolysis and acteoside upon partial acid hydrolysis (coTLC). The ^{1}H NMR of **8** showed, besides the presence of *trans*-caffeoyl and 3,4-dihydroxyphenylethyl moieties, three sugars due to three anomeric proton signals at $\delta 5.58$ (*d*, $J = 1.5$ Hz), 4.38 (*d*, $J = 7.9$ Hz) and 4.36 (*d*, $J = 7.5$ Hz) [Table 1]. The sequence of resonances of the sugar moiety with H-1 at $\delta 4.38$, traced first by ^{1}H–^{1}H COSY and then by one-bond ^{13}C–H COSY, were those of glucopyranose with shifts indicative of glycosylation and acylation at the C-3 and C-4 positions, respectively (H-3/C-3—$\delta 3.77/82.9$; H-4/C-4—$\delta 4.92/70.5$), as in the case of acteoside, e.g. [22]



8 (*trans*)

(Table 1). In turn, rhamnosyl signals, recognized in the same manner (H-1 at δ5.58), revealed deshielded NMR values for H-2 and C-2 (δ4.01 and 83.0, respectively), due to glycosylation at this position. The remaining ^{13}C signals were those of unsubstituted galactopyranosyl [23], the ^{1}H signals of which were located with the aid of ^{13}C–H COSY. Thus, rhamnose is attached to C-3 of glucose and galactose is a terminal sugar linked to C-2 of rhamnose. Moreover, the ^{1}H and ^{13}C NMR spectra of **8** contained series of much smaller signals with quite close, if not identical, shifts and coupling patterns, except for those assignable to *cis*-caffeoyl (olefinic protons doublets at δ5.76 and 6.88, with $J = 13$ Hz each) [21]. These signals could correspond to the minor compound having the same structure except the *cis*-configuration of the caffeic acid residue. This assumption was supported by the presence of 3,4-dihydroxyphenethyl, caffeoyl (*trans* plus *cis*), glucosyl, rhamnosyl and galactosyl moieties in equal amounts, in total, as judged by integrals in the ^{1}H NMR spectrum. Hence, **8** is 2^R-galactosylacteoside, a new naturally occurring product; we have named it lamalboside (either *trans* or *cis*).

Tiliroside, first found in *Tilia argentea* (Tiliaceae) [24] (structure revised in ref. [25]) and also in *Pteridium aquilinum* (Polypodiaceae) [26], *Quercus ilex* and *Q. cerris* (Fagaceae) [27, 28], *Helianthemum ovatum* (Cistaceae) [29], *Rubus chingii* (Rosaceae) [30] and *Rosa dauvarica* (Rosaceae) [31], has been already reported in the family Lamiaceae in *Phlomis spectabilis* [17], while kaempferol 3-*p*-coumaroylglucoside with an undefined ester linkage position was detected in *Phlomis purpurea* [32]. Generally, flavonoid *p*-coumaroylglucosides (of various aglycones) are considered as valuable chemotaxonomic markers in the Lamiaceae, restricted to some genera (e.g. *Phlomis*) of the subfamily Lamioideae [32] to which *Lamium* belongs.

Tiliroside has been only described as *trans*-isomer [17] and its susceptibility to *cis*/*trans* isomerization seems not to have been reported. *Trans*-*p*-coumaroyl esters of kaempferol and quercetin diglycosides and their *cis*-analogues have been described as pure compounds from *Strychnos variabilis* (Loganiaceae) [18], but without comments about possible isomerization. Transformation from *trans*- to *cis*-geometry was described for *p*-coumaroyl esters of some anthocyanins (from the Lamiaceae) [sun-induced] [33] and for alkyl ester of *p*-coumaric acid (UV-induced) [34].

Caffeoyl esters of di- and trisaccharide phenylethanoids, as well as chlorogenic acid, are typical for the family Lamiaceae [35]; however, lamalboside (**8**) now seems to be specific for *L. album*.

EXPERIMENTAL

Plant material. Flowers of *L. album* L. were collected at Dziewicza Góra near Poznań, Poland, in May 1992 and air-dried.

TLC. Cellulose MN-300 (Serva) in 15% HOAc (syst. 1). Polyamide 6D (Riedel-De Häehn) in H_2O–EtOH–Ac_2CH_2 4:2:1 (syst. 2); $CHCl_3$–MeOH–MeCOEt–Ac_2CH_2 9:4:2:1 (syst. 3); H_2O–*n*-BuOH–Me_2CO, 8:1:1 (syst. 4); EtOAc–EtOH–H_2O, 20:3:2 (syst. 5). Silica gel (Merck) in Me_2CO–*n*-BuOH–H_2O, 8:1:1 (syst. 6). Cellulose F, precoated (Merck) in 15% HOAc (syst. 7). 2D-TLC on cellulose plastic-backed sheets (without UV indicator) [Merck] in BAW (*n*-BuOH–HOAc–H_2O 4:1:5, upper phase) and 15% HOAc.

Spectroscopy. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were run with TMS as int. standard. UV spectra were recorded according to ref. [36].

Extraction and isolation. Plant material (15 g) was extracted with hot MeOH (×5). The dry extract was dissolved in H_2O, washed with $CHCl_3$ and sepd by prep. TLC (syst. 1) into bands 1–4 of increasing polarity. Band 3 yielded **1** + **2**, **3** + **4** and **5** by TLC in syst. 2. Compounds **1** + **2** sepd in syst. 7 gave **1** + **2** again from each band (*ca* 1 mg). Compound **3** (1.5 mg), **4** (1.2 mg) and **5** (1.6 mg) were purified in syst. 3. Band 4 was sepd in syst. 4 (×2 runs) to give **6** (155 mg), **7** (22 mg) and **8** (122 mg). Finally, **1–8** were purified by Sephadex LH-20 CC in MeOH. The sample (100 mg) of unknown flavonoid, obtained by cellulose CC in BAW in the work of ref. [5] from the flowers of *L. album*, was purified by successive CC on polyamide SC-6 (Macherey-Nagel) and Sephadex LH-20 in MeOH.

Hydrolysis. Using 1 M HCl, 90°. EtOAc extractions of hydrolysates were analysed for phenolics (see below) and H_2O residues for sugars (coTLC in syst. 6).

Table 1. ^1H and ^{13}C NMR data of lamalboside (**8**)* (in CD_3OD)

	trans-Isomer		*cis*-Isomer	
	C	H	C	H
Aglycone				
1	131.6	—	131.6	—
2	117.2	6.72, *d* (2.0)	117.2	6.72, *d* (2.0)
3	144.6	—	144.6	—
4	146.1	—	146.1	—
5	116.4	6.69, *d* (8.1)	116.4	6.69, *d* (8.1)
6	121.3	6.57, *dd* (2.0/8.1)	121.3	6.57, *dd* (2.0/8.1)
7	36.5	2.79, *t* (7.4)	36.5	2.79, *t* (7.4)
8	72.2	4.05, *m* 3.71, *m*	72.2	4.05, *m* 3.71, *m*
Caffeoyl				
1	127.7	—	128.1	—
2	115.3	7.07, *d* (2.0)	119.0	7.53, *d* (2.2)
3	149.8	—	148.6	—
4	146.8	—	145.6	—
5	116.6	6.79, *d* (8.3)	115.8	6.75, *d* (8.3)
6	123.3	6.96, *dd* (2.0/8.1)	125.9	7.11, *dd* (2.2/8.1)
7	148.0	7.60, *d* (16.0)	147.5	6.88, *d* (12.8)
8	114.7	6.28, *d* (16.0)	115.8	5.76, *d* (12.8)
9	168.3	—	166.8	—
Glucose				
1	104.1	4.38, *d* (7.9)	104.1	4.38, *d* (7.9)
2	76.2	3.39, *dd* (7.9/8.9)	76.0	‡
3	82.9	3.79, *t* (9)	83.2	‡
4	70.5	4.92, *t* (9)	70.5	‡
5	75.9	3.53 †	75.9	‡
6	62.3	3.58 †	62.3	‡
Rhamnose				
1	102.4	5.57, *d* (1.5)	102.4	5.55, *d* (1.5)
2	83.0	4.01, *dd* (1.5/3.6)	83.0	‡
3	71.8	3.66, *dd* (3.6/9.6)	71.8	‡
4	74.1	3.28, *t* (9.6)	74.2	‡
5	70.4	3.53, †	70.3	‡
6	18.5	1.06, *d* (6.1)	18.2	1.14, *d* (6.1)
Galactose				
1	107.5	4.36, *d* (7.5)	107.5	4.36, *d* (7.5)
2	72.9	3.56 †	72.9	‡
3	74.9	3.48, *dd* (9.5/3.2)	74.9	‡
4	70.5	3.80 †	70.5	‡
5	77.0	3.52 †	77.0	‡
6	62.9	3.85, *dd* (5.5/13.0) 3.72 †	62.9	‡

* Assignments made using ^1H–^1H COSY and one-bond ^1H–^{13}C COSY.

† Signal pattern unclear due to overlapping.

‡ Overlapped with other signals.

Trans- *and* cis-*Tiliroside* (*kaempferol* 3-O-*β*-(6‴-O-trans- and cis-p-*coumaroyl*)-*glucopyranoside*) [**1** + **2**]. Yellow powder. UV λ_{max}^{MeOH} nm: 268 sh, 300, 313, 358 sh; + NaOMe 277, 312 sh, 367; + NaOAc 275, 312, 370; + H_3BO_3 + NaOAc 270, 314, 360 sh; + $AlCl_3$ 275, 308, 402 sh; + $AlCl_3$ + HCl 276, 308, 400 sh. ^1H NMR (CD_3OD): [component **1** = *trans*-isomer] δ 7.99 and 6.82 (each 2H, AA′BB′, J_{ortho} = 8.7 Hz, H-2′, 6′ and H-3′, 5′, respectively), 7.40 and 6.07 (each 1H, *d*, *J* = 15.6 Hz, H-7‴ and H-8‴, respectively), 7.32 and 6.80 (each 2H, AA′BB′, J_{ortho} = 8.4 Hz, H-2‴, 6‴ and H-3‴, 5‴, respectively), 6.31 and 6.13 (each 1H, *d*, *J* = 2.1 Hz, H-8 and H-6, respectively), 5.23 (1H, *d*, *J* = 7.5 Hz, H-1″), 4.30 (1H, *dd*, *J* = 2.0/11.9 Hz, H-$6''_A$), 4.18 (1H, *dd*, *J* = 6.3/11.9 Hz, H-$6''_B$), 3.5–3.2 (*m*, H-2″–5″); [component **2** = *cis*-isomer] 7.96 and 6.80 (each 2H, AA′BB′, J_{ortho} = 8.0 Hz, H-2′, 6′

and H-3′, 5′, respectively), 7.51 and 6.68 (each 2H, AA′BB′, $J_{\mathrm{ortho}} = 8.7$ Hz, H-2‴, 6‴ and H-3‴, 5‴, respectively), 6.71 and 5.50 (each 1H, *d*, $J = 12.6$ Hz, H-7‴, H-8‴, respectively), 6.18 and 6.03 (each 1H, *d*, $J = 2.0$ Hz, H-8 and H-6, respectively), 5.19 (1H, *d*, $J = 7.5$ Hz, H-1″), 4.29 (1H, *m*, H-$6''_A$), 4.18 (1H, *m*, H-H-$6''_B$). The ratio *cis/trans* was *ca* 1:5 from integrals. Hydrolysis (1 hr) gave kaempferol, *p*-coumaric acid (coTLC, systs 1, 3) and glucose.

Trans-*tiliroside* (**1**). Obtained by ref. [5]. Yellow powder. 2D-TLC: R_fs: BAW: 0.92, 15% HOAc: 0.27 (*trans*), 0.37 (*cis*). The MeOH soln of **1** on exposure to daylight showed by 1D TLC on cellulose in 15% HOAc increasing amounts of *cis*-isomer as a higher migrating spot. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 267, 300sh, 316, 358sh; + NaOMe 275, 312sh, 370; + NaOAc 275, 312, 373; + H_3BO_3 + NaOAc 267, 316, 360sh; + $AlCl_3$ 275, 308, 322sh, 402; + $AlCl_3$ + HCl 276, 306, 322sh, 401. ^{1}H NMR (DMSO-d_6): δ12.60 (1H, *sharp s*, 5-OH), 10.87, 10.18, 10.06 (each 1H, *br s*, OH at C-7, C-4′, C-4‴), 8.02 and 6.88 (each 2H, AA′BB′, $J_{\mathrm{ortho}} = 8.9$ Hz, H-2′, 6′ and H-3′, 5′, respectively), 7.39 and 6.81 (each 2H, AA′BB′, $J_{\mathrm{ortho}} = 8.8$ Hz, H-2‴, 6‴ and H-3‴, 5‴, respectively), 7.37 and 6.14 (each 1H, *d*, $J = 16.0$ Hz, H-7‴ and H-8‴, respectively), 6.41 and 6.18 (each 1H, *d*, $J = 2.1$ Hz, H-8 and H-6, respectively), 5.50 (1H, *d*, $J = 4.1$ Hz, sugar OH), 5.48 (1H, *d*, $J = 7.5$ Hz, H-1″), 5.27 (1H, *d*, $J = 5.7$ Hz, sugar OH), 5.23 (1H, *d*, $J = 5.3$ Hz, sugar OH), 4.30 (1H, *dd*, $J = 2/11.7$ Hz, H-$6''_A$), 4.06 (1H, *dd*, $J = 6.3/11.7$ Hz, H-$6''_B$), 3.35–3.20 (*m*, H-2″–5″); OH signals were removed after addition of D_2O. ^{13}C NMR (DMSO-d_6): [kaempferol moiety] δ156.4 (C-2), 133.0 (C-3), 177.3 (C-4), 161.1 (C-5), 98.7 (C-6), 164.1 (C-7), 93.6 (C-8), 156.3 (C-9), 103.8 (C-10), 120.7 (C-1′), 130.0 (C-2′, 6′), 115.7 (C-3′, 5′), 159.9 (C-4′), [glucosyl moiety] 100.9 (C-1″), 74.2 (C-2″), 76.2 (C-3″), 69.9 (C-4″),74.0 (C-5″), 62.9 (C-6″), [*p*-coumaroyl moiety] 124.8 (C-1‴), 130.7 (C-2‴, 6‴), 115.0 (C-3‴, 5‴), 159.7 (C-4‴), 144.5 (C-7‴), 113.6 (C-8‴), 166.1 (C-9‴).

Acteoside (trans + cis) (**7**). Off-white amorphous powder. ^{1}H NMR (CD_3OD): (*trans*-component) [aglycone moiety] δ6.69 (1H, *d*, $J = 1.8$ Hz, H-2), 6.67 (1H, *d*, $J = 8.4$ Hz, H-5), 6.56 (1H, *dd*, $J = 1.8/8.4$ Hz, H-6), 4.05 (1H, *m*, H-8_A), 3.73 (1H, *dd*, $J = 5.3/7.8$ Hz, H-8_B), 2.79 (2H, *t*, $J = 7.8$ Hz, H-7), [caffeoyl moiety] 7.59 and 6.27 (each 1H, *d*, $J = 15.9$ Hz, H-7 and H-8, respectively), 7.05 (1H, *d*, $J = 2.1$ Hz, H-2), 6.96 (1H, *dd*, $J = 2.1/8.4$ Hz, H-6), 6.78 (1H, *d*, $J = 8.4$ Hz, H-5), [glucosyl moiety] 4.92 (1H, *t*, $J = 9.3$ Hz, H-4), 4.37 (1H, *d*, $J = 7.8$ Hz, H-1), 3.81 (1H, *t*, $J = 9.3$ Hz, H-3), 3.61 (1H, *m*, H-6_A), 3.55 (1H, *m*, H-6_B), 3.39 (1H, *dd*, $J = 7.8/9.3$ Hz, H-2), [rhamnosyl moiety] 5.18 (1H, *d*, $J = 1.8$ Hz, H-1), 3.91 (1H, *dd*, $J = 1.8/3.0$ Hz, H-2), 3.58 (1H, *dd*, $J = 3.0/9.6$ Hz, H-3), 3.53 (1H, *dq*, $J = 9.6/6.0$ Hz, partially overlapped H-5), 3.30 (1H, *t*, $J = 9.6$ Hz, H-4), 1.09 (3H, *d*, $J = 6.0$ Hz, H-6). (*cis*-Component) [aglycone moiety] like in *trans*-isomer; [caffeoyl moiety] 7.52 (1H, *d*, $J = 2.1$ Hz, H-2), 7.10 (1H, *dd*, $J = 2.1/8.4$ Hz, H-6), 6.87 and 5.76 (each 1H, *d*, $J = 13.0$ Hz, H-7 and H-8, respectively), 6.73 (1H, *d*, $J = 8.4$ Hz, H-5), [glucosyl moiety] 4.92 (1H, *t*, $J = 9.3$ Hz, H-4), 4.35 (1H, *d*, $J = 7.5$ Hz, H-1), [rhamnosyl moiety] 5.16 (1H, *d*, $J = 1.8$ Hz, H-1), 1.18 (3H, *d*, $J = 6.3$ Hz, H-6). *trans/cis* Ratio was *ca* 6/1. ^{13}C NMR (CD_3OD): δ [*trans/cis*] [aglycone moiety] the same for 2 isomers 131.5 (C-1), 116.4 (C-2), 144.7 (C-3), 146.2 (C-4), 117.2 (C-5), 121.3 (C-6), 36.6 (C-7), 72.3 (C-8), [caffeoyl moiety] 127.7/128.1 (C-1), 114.8/119.0 (C-2), 149.8/148.4 (C-3), 146.9/145.7 (C-4), 116.6/115.8 (C-5), 123.2/125.9 (C-6), 148.0/147.4 (C-7), 115.3/115.7 (C-8), 168.3/166.9 (C-9), [glucosyl moiety] 104.3/104.3 (C-1), 76.1/76.0 (C-2), 81.7/81.9 (C-3), 70.5/70.5 (C-4), 76.3/76.2 (C-5), 62.4/62.4 (C-6), [rhamnosyl moiety] 103.1/103.1 (C-1), 72.4/72.4 (C-2), 72.13/72.18 (C-3), 73.86/73.90 (C-4), 70.7/70.4 (C-5), 18.5/18.2 (C-6).

Lamalboside (*2-(3,4-dihydroxyphenyl)ethyl* O-β-D-galactopyranosyl-(1 → 2)-α-L-*rhamnopyranosyl*-(1 → 3)-4-O-trans- *and* cis-*caffeoyl-β*-D-*glucopyranoside*) (**8**). Off-white amorphous powder. $[\alpha]_D$ 44.9° (MeOH; *c* 0.49). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 203 (4.61), 220 (4.23), 231 (4.07), 248 (3.95)sh, 292 (4.04), 300 (4.05), 332 (4.18); + NaOMe 258, 312, 381; + NaOAc 251sh, 288, 342, 380sh; + H_3BO_3 + NaOAc 284, 355sh, 384; + $AlCl_3$ 264, 303sh, 364; + $AlCl_3$ + HCl the same as in MeOH. ^{1}H and ^{13}C NMR data: Table 1. Hydrolysis: (i) total (3 hr) gave caffeic acid (coTLC in systs 4 and 5) and galactose, glucose and rhamnose; (ii) partial (0.5 hr), then prep. TLC in syst. 5 (run × 2) gave acteoside (= **7**) (R_f 0.46) (coTLC, systs 4 and 5).

Acknowledgements—The authors are grateful to Dr A. Krupińska (our Department) and Prof. K. Latowski (A. Mickiewicz University, Poznań) for collection and identification of plant material, Prof. I. Calis (Hacettepe University) for the sample of verbascoside and Prof. Dr H. C. B. Borkowski (Warsaw) for supplying a sample of unidentified flavonoid from *L. album*. The isolation work was a part of Miss H. Cichocka's M.S. degree performed at our Department.

REFERENCES

1. Weiss, R. F. (1988) in *Herbal Medicine*, pp. 313–314. Beaconsfield, Beaconsfield.
2. Penso, G. (1983) in *Index Plantarum Medicinalium Totius Mundi Corumque Synonymorum*, p. 549. O.E.M.F. Milano.
3. Harborne, J. B. (1967) *Phytochemistry* **6**, 1569.
4. Kwaśniewski, W. (1959) *Planta Med.* **7**, 35.
5. Duchnowska, A. and Borkowski, B. (1964) *Dissert. Pharm.* **16**, 91.
6. Damtoft, S., Jensen, S. R. and Nielsen, B. J. (1992) *Phytochemistry* **31**, 135.
7. Damtoft, S. (1992) *Phytochemistry* **31**, 175.
8. Duchnowska, A. and Borkowksi, B. (1964) *Dissert. Pharm.* **16**, 101.
9. Góra, J., Świątek, L., Kurowska, A., Kalemba, D. and Boruch, T. (1983) *Acta Polon. Pharm.* **40**, 389.
10. Hegnauer, R. (1989) in *Chemotaxonomie der Pflanzen* pp. 609–611. Bd 8. Birkhäuser, Basel.
11. Hegnauer, R. (1966) in *Chemotaxonomie der Pflanzen* pp. 336–337. Bd 4. Birkhäuser, Basel.

12. Kory, M., Hodisan, V., Toader, S. and Gugu, P. (1982) *Clujul Med.* **55**, 156; *Chem. Abstracts* (1983) **98**, 46 480.
13. Budzianowski, J., Skrzypczak, L. and Wesołowska, M. (1990) *Sci. Pharm.* **58**, 15.
14. Budzianowski, J. (1991) *J. Chromatogr.* **540**, 469.
15. Cheminat, A., Zawatzky, R., Becker, H. and Brouillard, R. (1988) *Phytochemistry* **27**, 2787.
16. Budzianowski, J. (1991) *Planta Med.* **57**, 399.
17. Kumar, R., Bhan, S., Kalla, A. K. and Dhar, D. L. (1985) *Phytochemistry* **24**, 1124.
18. Brasseur, T. and Angenot, L. (1988) *Phytochemistry* **27**, 1487.
19. Markham, K. R. and Chari, M. (1982) in *The Flavonoids: Advances in Research* (Harborne, J. B. and Mabry, T. J., eds), p. 40. Chapman and Hall, London.
20. Harborne, J. B. (1982) *Phytochemical Methods*, Chapman and Hall, London.
21. Nishimura, H., Sasaki, H., Inagaki, N., Chin, M. (Zhengxiong, Ch.) and Mitsuhashi, H. (1991) *Phytochemistry* **30**, 965.
22. Debrauwer, L., Maillard, C., Babadjamian, A., Vidal-Ollivier, E., Laget, M., Salmona, G. and Afzal-Raffi, Z. (1989) *Pharm. Acta Helv.* **64**, 183.
23. Shoyama, Y., Matsumoto, M. and Nishioka, J. (1987) *Phytochemistry* **26**, 983.
24. Hörhammer, Z., Stich, Z. and Wagner, H. (1961) *Archiv Pharm.* **294**, 685.
25. Harborne, J. B. (1964) *Phytochemistry* **3**, 151.
26. Wang, C.-Y., Pomukcu, A. M. and Bryan, G. T. (1973) *Phytochemistry* **12**, 2298.
27. Romussi, G., Cafaggi, S. and Bignardi, G. (1982) *Pharmazie* **37**, 738.
28. Romussi, G., Ciarallo, G. and Parodi, B. (1982) *Pharmazie* **43**, 294.
29. Pijewska, L. and Kamecki, J. (1977) *Rocz. Chem.* **51**, 291.
30. Hattori, M., Kuo, K.-P., Shu, Y.-Z., Tezuka, Y., Kikuchi, T. and Namba, T. (1988) *Phytochemistry* **27**, 3975.
31. Kuang, H.-X., Kasai, R., Ohtani, K., Liu, Z.-Sh., Yuan, C.-S. and Tanaka, O. (1989) *Chem. Pharm. Bull.* **37**, 2232.
32. Tomas-Barberan, F. A., Gill, M. I., Ferreres, F. and Tomas-Lorente, F. (1992) *Phytochemistry* **32**, 3097.
33. Saito, N. and Harborne, J. B. (1992) *Phytochemistry* **31**, 3009.
34. Hashidoko, Y., Tahara, S. and Mizutani, J. (1992) *Phytochemistry* **31**, 3282.
35. Molgaard, P. and Ravn, H. (1988) *Phytochemistry* **27**, 2411.
36. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, Springer, New York.