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THREE NEW 5,10-EPOXYGERMACRANOLIDES FROM *LIATRIS CHAPMANII* AND *LIATRIS GRACILIS**

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Key Word Index—*Liatris chapmanii*; *L. gracilis*; Compositae; sesquiterpene lactones; 5,10-epoxygermacranolides; benzofuran; euparin; methylated flavones.

Abstract—Examination of *Liatris chapmanii* (T + G) Kuntze led to the isolation of two new germacranolides, chapliatrin (**1a**) and isochapliatrin (**1b**). *Liatris gracilis* Pursh gave chapliatrin and acetylchapliatrin (**1c**). The stereochemistry assigned to C-3, C-4 and C-10 is tentative. All three compounds possess the hitherto-unreported 5,10-oxygen linkage. *L. gracilis* also gave the benzofuran euparin (**2**) and the flavones hispidulin (dinatin, **3a**) and 3′,6-dimethoxy-4′,5,7-trihydroxyflavone (**3b**). *L. chapmanii* also gave 5-hydroxy-3′,4′,6,7-tetramethoxyflavone (**3c**).

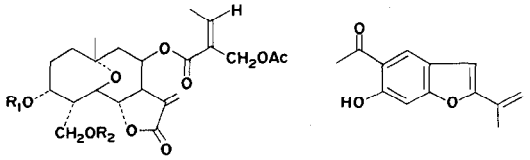
INTRODUCTION

As part of a chemical investigation of the genus *Liatris* [1–6], we examined *Liatris chapmanii* (T + G) Kuntze and *L. gracilis* Pursh, both common in the vicinity of Tallahassee. The present communication deals with the isolation and structure determination of three closely related germacranolides which we have named chapliatrin (**1a**), isochapliatrin (**1b**) and acetylchapliatrin (**1c**) [7]. Limited amounts of material and inconclusive results combined with formation of uncharacterizable product mixtures in the reactions to which these substances were subjected forced us to rely mainly on spectral evidence in the structure elucidation process. Incidentally, we were unable to isolate from our collections of *L. chapmanii* the sesquiterpene lactone liatrin (**4**) previously reported by Kupchan *et al.* [8].

RESULTS

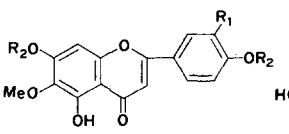
Chapliatrin (**1a**), $C_{24}H_{32}O_{10}$ (high resolution MS), was isolated from *L. chapmanii* and *L. gracilis* and could not be induced to crystallize. It was a conjugated γ-lactone (IR bands at 1760 and 1640 cm^{-1}, strong UV end absorption) and contained two acetates (IR band at 1720 cm^{-1}, two three proton resonances at 2·01 and 2·10 ppm, MS) and a hydroxyl group (IR spectrum, conversion to a triacetate).

The NMR spectrum (Table 1) also contained the typical doublets due to H_a and H_b of an exocyclic methylene group conjugated with a lactone, as in partial structure A. Spin decoupling experiments involving H_a and H_c established the location of the H_c multiplet at 3·33 ppm. Irradiation

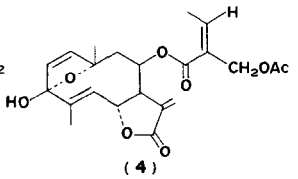


(**1a**) R_1 = H, R_2 = Ac
(**1b**) R_1 = Ac, R_2 = H
(**1c**) R_1, R_2 = Ac

(**2**)



(**3a**) R_1, R_2 = H
(**3b**) R_1 = OMe, R_2 = H
(**3c**) R_1 = H, R_2 = Me



(**4**)

* Part 9 in a series *Constituents of* Liatris *Species*. For part 8 see Herz, W. and Sharma, R. P. (1975) *J. Org. Chem.* **40**, 392.

Table 1. ^{1}H-NMR spectra

Compound	H-1	H-2†	H-3	H-4	H-5	H-6	H-7
1a	1·37*ddbr* (15,5, ~ 1) 2·72*ddbr* (15,9,2)	~ 2‖	4·69*br*§	2·22*m*¶	4·00*dd* (10,4)	5·71*t* (10)	3·33*m*
1b	1·44*ddbr* (15,5, ~ 1) 2·55*ddbr* (15,9,2)	~ 2‖	5·50*br*	2·38*m*¶	4·00*dd* (10,4)	5·38*t* (10)	3·42*m*
1c	1·40*ddbr* (15,5, ~ 1) 2·35*m*	~ 2‖	5·40*br*	2·35*m*§¶	4·03*dd* (10,4)	5·48*t* (10)	3·41*m*

* Run at 270 MHz in $CDCl_3$ soln on a Bruker HFX-270 instrument with TMS as internal standard. Values are in ppm; *d*, doublet; *t*, triplet; *q*, quartet; *br*, broadened singlet; *m*, multiplet. Unmarked signals are singlets. Figures in parentheses are coupling constants in Hz.

† Intensity two protons.

‡ Intensity three protons.

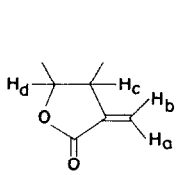
at the frequency of H_c collapsed a triplet at 5·71 ppm to a doublet and a broadened peak at 5·84 ppm into a doublet of doublets. Although the chemical shift difference of these two signals was not great, comparison with similar multiplets in the spectra of **1b** and **1c** (Table 1) indicated that the triplet of higher frequency was that of H_d, the proton under the lactone, and that the broad singlet at lower frequency could be assigned to proton H_c, a proton under an ester function [9].

Since all but one of the 10 oxygen atoms had been accounted for, the remaining oxygen had to be part of an ether linkage.

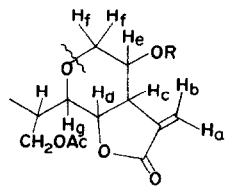
The identity of the seven carbon ester side was revealed by the NMR spectrum which contained a vinyl methyl doublet (*J* 7) at 2·15 ppm, coupled to a slightly broadened quartet centered at 6·51 ppm. This in turn was long range coupled to a two proton broadened singlet (superposed on the signal of >C<u>H</u>–OH which could be shifted downfield on acetylation—see Table 1). These results indicated an acetylsarracinoyl side chain as in liatrin (**4**) [8] and some other lactones of *Liatris* species [5, 6]. This was supported by the high resolution MS which showed, *inter alia*, strong peaks at *m/e* 322 ($C_{17}H_{22}O_6$, 8·2%, corresponding to the loss of a unit of mass 158), *m/e* 141 ($C_7H_9O_3$, 33·5%) and *m/e* 99 ($C_5H_7O_2$, 15·2%).

Irradiation at the frequency of H_c sharpened the H_c signal and also affected some signals partially buried under the acetates and the vinylic methyl, presumably the signals of H_f since the multiplicity of H_c indicated that it was adjacent to a methylene group. Conversely, irradiation in this region converted the H_d resonance into a sharp narrowly-split doublet (for other effects, *vide infra*).

H_d at 5·71 ppm was found coupled to a doublet of doublets at 4·00 ppm (H_g). The chemical shift of the latter suggested that it was the signal of a proton on carbon carrying an oxygen atom. The second coupling of H_g could be related to a multiplet (H_h) at 2·22 ppm which was also coupled to an AB system (of –C<u>H</u>$_2$OAc) centered at 4·13 ppm. Consequently, A could be expanded to partial structure B. Irradiation at the frequency of H_h sharpened the >C<u>H</u>–OH signal of **1a** (H_i) at 4·69 ppm buried under the –C<u>H</u>$_2$OAc signal of the side chain, but nicely visible at 5·40 ppm (as >C<u>H</u>OAc) in the spectrum of the acetate **1c**. Spin-decoupling at the frequency of H_i in turn not only affected the H_h signal, but caused some changes in the signals (total intensity four protons) buried under the acetates and the vinyl methyl. Since two of the four protons in this



A



B

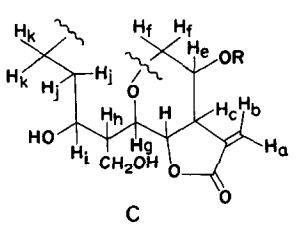
of chapliatrin and congeners*

H-8	H-9†	H-13	H-14‡	H-15†	H-3′	H-4′‡	H-5′	Ac‡
5·84*br* (5,2·5,2)	~2‖	6·28*d* (3·2) 5·61*d* (3·0)	1·27*br***	4·13††	6·51*q* (7)	2·15*d* (7)	4·69§	2·01 2·10
5·82*br* (5,2·5,2)	~2‖	6·30*d* (3·3) 5·60*d* (3·0)	1·28*br*	3·68††	6·51*q* (7)	2·15*d* (7)	4·70‡‡	2·00 2·12
5·82*br* (5,2·5,2)	~2‖	6·29*d* (3·3) 5·59*d* (3·0)	1·25*br*	4·34††	6·52*q* (7)	2·15*d* (7)	4·70‡‡	1·99 2·01 2·10

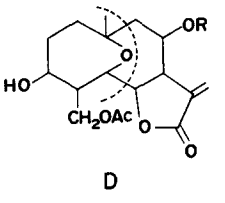
‖ Observed signal.
§ Superimposed signal.
† $J_{3,4} = 3$, $J_{4,5} = 4$, $J_{4,15} = 7$ Hz.
** Broadening due to coupling to H-9.
†† AB of ABX system.
‡‡ AB system.

region were already accounted for by H_f (*vide supra*), and since the NMR spectrum contained only three additional signals, i.e. a slightly broadened methyl singlet at 1·27 and two gem-coupled (J 15) one proton multiplets at 1·37 and 2·72 ppm, the empirical formula required that the two remaining protons whose signals appear in the 2 ppm region constitute a methylene group (H_j) adjacent to H_i. Now irradiation at the frequencies of H_f and H_j affected not only the H_e resonance, but also collapsed the multiplets at 1·37 and 2·72 ppm to two mutually coupled doublets, hence the latter must be associated with a methylene group (H_k) and the formula of chapliatrin could be expanded to C.

To account for the multiplicity of the $-CH_2-$ signals, the carbon carrying the methyl group responsible for the methyl singlet at 1·27 ppm must be placed adjacent to it and must serve as the second terminus of the oxide linkage, thus leading unequivocally to formula **1a** (devoid of stereochemistry). This formula is also biogenetically plausible and accounts for the chemical shift of the C-10 methyl signal, its broadening due to long-range coupling to H_f and the appearance, in the high resolution MS of **1a** and **1b** of an ion $C_{10}H_{15}O_4$ (8·2 and 40·8%) which probably arises from the cleavage shown in D, since it was not exhibited by acetylchapliatrin (**1c**). The latter whose formation from **1a** required relatively stringent conditions (see Experimental) was identical in all respects (mmp, TLC, spectral behavior) with naturally-occurring material, mp 143°, isolated from *L. gracilis*.



C



D

Isochapliatrin, $C_{29}H_{32}O_{10}$ (MS), mp 162–162·5°, was isolated from *L. chapmanii*. Its NMR spectrum exhibited small but obvious differences from that of **1a** (see Table 1) which could be traced to formula **1b**. This supposition was confirmed by extensive spin decoupling experiments analogous to those described for **1a** and by acetylation, under mild conditions (acetylation of a primary hydroxyl group) to **1c**.

The stereochemistry at C-5, C-6, C-7 and C-8 shown in the formulas has been deduced as follows. If the usual assumption is made that the C-7 side chain is equatorial and β as in all sesquiterpene lactones of authenticated stereochemistry, the values of $J_{5,6}$ and $J_{6,7}$ given in Table 1 require that H-5 be *trans* to H-6 and α and that H-6 be *trans* to H-7 and β, i.e. that the lactone ring be *trans*-fused. This conclusion is reinforced by the magnitude of $J_{7,13a}$ and $J_{7,13b}$ (>3 Hz) which according to Samek's rule [10] indicates the presence of a *trans*-lactone ring and by the CD curves which display negative Cotton effects

Table 2. ^{13}C-NMR spectra of chapliatrin and congeners

Signal no.	1a*	1b*	1c†	Assignment
1	172·3*s*	171·4*s*	170·2*s*	C=O (C-12 and acetates)
2	171·8*s*	170·6*s*	169·9*s*	
3	169·9*s*	169·4*s*	169·8*s*	
4			168·4*s*	
5	165·3*s*	164·8*s*	164·4*s*	C-1′
6	147·6*d*	146·9*d*	145·6*d*	C-3′
7	135·6*s*	135·3*s*	135·0*s*	C-11
8	127·5*s*	127·4*s*	127·4*s*	C-2′
9	122·0*t*	121·6*t*	121·0*t*	C-13
10	79·9*s*	79·4*s*	79·4*s*	C-10
11	78·1*d*	78·1*d*	78·1*d*	C-5
12	77·9*d*	77·8*d*	77·4*d*	C-6
13	68·1*d*	71·4*d*	70·9*d*	C-3
14	67·3*d*	67·4*d*	67·4*d*	C-8
15	66·2*t*	65·3*t*	64·9*t*	C-5′
16	63·3*t*	60·2*t*	61·6*t*	C-15
17	49·9*d*	52·1*d*	48·7*d*	C-4
18	47·6*d*	47·2*d*	47·2*d*	C-7
19	45·7*t*	45·5*t*	45·5*t*	C-9
20	30·2*t*	31·4*t*	31·3*t*	C-1
21	30·7*q*	30·6*q*	30·5*q*	C-14
22	29·8*t*	27·0*t*	26·6*t*	C-2
23	21·0*q*	21·1*q*	20·9*q*	
24	20·9*a*	20·9*q*	20·7*q*	Ac
25			20·6*q*	
26	16·0*q*	15·9*q*	15·8*q*	C-4′

* Run in $CDCl_3$ on Varian XL 100 instrument.
† Run in $CDCl_3$ on Bruker HFX-270 MHz instrument.

near 260 nm [11]. The relatively small value of $J_{7,8}$ (2 Hz) then requires that H-8 be equatorial and α, i.e. that the ester side chain be β-oriented. Thus the stereochemistry of chapliatrin and its congeners at C-6 and C-8 is the same as that of all previously-isolated sesquiterpene lactones in *Liatris* species [1, 2, 4–6, 8].

The somewhat speculative stereochemistry assigned to the remaining centers (C-3, C-4 and C-10) has been arrived at by comparison of observed coupling constants with our best estimate of coupling constants deduced with the aid of molecular models and will require verification or correction by work now in progress. If the proposal is correct, the model suggests the existence of strong NOE's as the result of interaction between the C-10 methyl group and H-4 and H-6. However, the proximity of the H-4 resonance to the vinyl methyl and acetate signals, on the one hand, and the H-6, H-8 and H-13b signals on the other and line broadening interfered with the appropriate experiments.

The ^{13}C-NMR spectra listed in Table 2 are fully consonant with the proposed structures. Assignments of frequencies to the various carbonyl carbons, to C-10, C-11 and C-2′ are based on predicted shifts [13, 14] and comparisons with data in the literature [15]. Signals of C-7, C-13, C-14, C-15, C-3′, C-4′ and C-5′ and the acetate methyls were identified by single frequency decoupling. Irradiation at the frequency of (superimposed) H-3 and H-5 collapsed doublets at 78·9 and 68·1 ppm (in **1a**); that the resonance at higher field was that of C-3 was established by its shift to lower field on acetylation to **1b** and **1c** (α-effect). Irradiation at the frequency of (almost superimposed) H-6 and H-8 collapsed doublets at 77·9 and 67·3 ppm (in **1a**); of the two, the C-6 signal is predicted to occur at lower field. Irradiation at the frequency of (superimposed) H-1, H-2, H-4 and H-9 collapsed a doublet at 49·9 and three triplets at 45·7, 30·2 and 29·8 ppm (in **1a**); hence the doublet must be assigned to C-4. This is corroborated by its expected upfield shift on deacetylation to **1b** (β-effect). Furthermore, the upfield shift of the 29·8 ppm triplet to 27·0 (in **1b**) and 26·6 ppm (in **1c**) permits its unambiguous assignment to C-2. Lastly a distinction between the C-1

and C-9 signals is possible because the former is predicted to occur at lower field.

Three other fractions from the chromatography of the *L. gracilis* extract gave yellow solids which were identified as euparin (**2**), [16] hispidulin (dinatin, **3a**) [17] and 3′,6-dimethoxy-4′,5,7-trihydroxyflavone [18]. *L. chapmanii* gave 5-hydroxy-3′,4′,6,7-tetramethoxyflavone (**3c**) [19].

EXPERIMENTAL

Extraction of Liatris chapmanii. Above ground parts of *Liatris chapmanii* (T + G) Kuntze, collected by Dr. R. K. Godfrey in the vicinity of Tallahassee in October 1968, was extracted with $CHCl_3$ and worked up in the usual fashion [20]. The crude gum, wt. 30 g, was chromatographed over 450 g of silicic acid (Mallinckrodt 100 mesh), 500 ml fractions being eluted in the following order: fractions 1–16 (C_6H_6), 17–30 (C_6H_6–$CHCl_3$ 4:1), 31–46 (C_6H_6–$CHCl_3$ 1:1), 47–60 (C_6H_6–$CHCl_3$ 1:4), 61–70 ($CHCl_3$). Fractions 8 and 9 (wt. 0·466 g) were solid. Recrystallization from EtOAc–hexane afforded crystalline 5-hydroxy-3′,4′,6,7-tetramethoxyflavone, mp 194·5–195·5°; lit. 189–190, 190–191° [19], MW (MS) 358, PMR signals ($CDCl_3$) at 12·76 (5-OH), 6·67 and 6·64 (H-3 and H-8), 7·56*dd* (8·5, 2, H-6′), 7·37*d* (2, H-2′), 7·01*d* (8·5, H-5′), 3·99, 3·98, 3·97, 3·92 ppm (4 methoxyls), UV (MeOH) λ_{max} 213 (16800), 245 (9700, sh at 252), 277 (10900), 340 nm (16500), (MeOH–$AlCl_3$) 216 (17900), 238 (7200), 260 (8900), 292 (11800), 366 nm (16800), (MeOH–$AlCl_3$, HCl) 217 (16800), 238 (7200), 259 (8600), 292 (11800), 362 nm (16100). There was a slight m.p. depression on admixture of an authentic sample* of mp 190–191°, but the PMR, IR and UV spectra (MeOH, MeOH–$AlCl_3$, MeOH–$AlCl_3$–HCl) were superimposable. Fractions 14–36 (wt. approx. 9 g) showed one major spot on TLC and were combined. Rechromatography of a 1 g portion over Si gel afforded 0·64 g of chapliatrin (**1a**) as a gum, $[\alpha]_{Hg}^{22}$ −35°; CD curve $[\theta]_{265}$ −860, $[\theta]_{235}$ +1290, $[\theta]_{213}$ −45200 (last reading); IR bands at 3480 (hydroxyl), 1760, 1720 and 1640 cm^{-1}; UV strong end absorption at 220 nm; high resolution mass spectrum *m/e* (composition, %) 480 (M^+, $C_{24}H_{32}O_{10}$, very weak), 462 ($C_{24}H_{30}O_9$, 0·4), 420 ($C_{22}H_{28}O_8$, 0·9), 360 ($C_{20}H_{24}O_6$, 0·4), 323 ($C_{17}H_{23}O_6$, 4·6), 322 ($C_{17}H_{22}O_6$, 8·2), 280 ($C_{15}H_{20}O_5$, 2·4), 263 ($C_{17}H_{23}O_6$, 3·2), 262 ($C_{15}H_{18}O_4$, 6·9), 244 ($C_{15}H_{16}O_3$, 4·1), 199 ($C_{10}H_{15}O_4$, 8·2), 141 ($C_7H_9O_3$, 33·5), 99 ($C_5H_7O_2$, 15·2), 81 (C_5H_5O, 29·3). (Calc. for $C_{24}H_{32}O_{10}$: C, 59·99; H, 6·71; O, 33·30. Found: C, 60·13; H, 6·73; O, 32·74). Acetylation of **1a** with C_5H_5N–Ac_2O in the usual fashion resulted in recovery of starting material. Acetylation of 0·1 g of **1a** with 0·05 g of toluenesulfonic acid and 1 ml Ac_2O at room temp. overnight, decomposition with iced H_2O, extraction with $CHCl_3$, washing of the extract with bicarbonate soln and H_2O and drying gave, after removal of solvent, a gum (0·09 g). Recrystallization from hexane–EtOAc gave solid acetylchapliatrin (**1c**), mp 142–144°, identical with natural **1c** from *L. gracilis* (*vide infra*). Fractions 42–53 (wt. approx. 5 g) which showed one major spot on TLC were combined. Recrystallization from EtOAc–hexane afforded 0·97 g crystalline isochapliatrin (**1b**) (more could be recovered from the mother liquor), mp 162–162·5°, $[\alpha]_D$ −74·1° (C 11·6 mg/ml) CD curve $[\theta]_{265}$ − 1300, $[\theta]_{242}$ + 288, $[\theta]_{230}$ − 3890 (last reading); IR bands at 3530 (hydroxyl), 1770 and 1672 (conjug. γ-lactone), 1743 (acetates), 1715 and 1642 cm^{-1} (conjug. ester), UV λ_{max} 208 nm (18400); high resolution mass spectrum *m/e* (composition, %) 480 (M^+, $C_{24}H_{32}O_{10}$, very weak), 420 ($C_{22}H_{28}O_8$, 5·2), 361 ($C_{20}H_{26}O_6$, 2·0), 360 ($C_{20}H_{24}O_6$, 1·1), 323 ($C_{17}H_{23}O_6$, 10), 322 ($C_{17}H_{22}O_6$, 12·4), 263 ($C_{15}H_{19}O_4$, 13·2), 262 ($C_{15}H_{18}O_4$, 29·5), 244 ($C_{15}H_{16}O_3$, 10·4), 199 ($C_{10}H_{15}O_4$, 40·8), 141 ($C_7H_9O_3$, 100), 99 ($C_5H_7O_2$, 76·5), 81 (C_5H_5O, 21·1). (Calcd. for $C_{24}H_{32}O_{10}$: C, 59·99; H, 6·71; O, 33·30. Found: C, 59·91; H, 6·93; O, 32·61). Acetylation of 0·075 g of **1b** with Ac_2O–C_5H_5N afforded **1c**, identical with material from *L. gracilis*.

A second collection of *L. chapmanii* (Lazor no. 5591, collected on Sept. 25, 1971 5 miles west of Tallahassee along State Road 20), wt. 7·8 kg, furnished only 20 g of gum in the $CHCl_3$ extract. Chromatography in the usual fashion afforded no fractions that were homogeneous on TLC. None of the several constituents could be identified definitely as **1a**, **1b**, **1c** or **4**.

Extraction of Liatris gracilis. Above-ground parts of *Liatris gracilis* Pursh, wt. 10 kg, collected by Mr. R. A. Lazor on 25 September 1971, 3 miles east of the intersection of US 98 and Alligator Harbor Road, Franklin County, Florida (Lazor no. 5590) was extracted with $CHCl_3$ and worked up in the usual manner. The crude gum, wt. 25 g, was chromatographed over 500 g of silicic acid, 500 ml fractions being collected in the following order: 1–3 (C_6H_6), 4–5 (C_6H_6–$CHCl_3$, 3:1), 6–10 (C_6H_6–$CHCl_3$ 1:1), 11–25 ($CHCl_3$), 26–28 ($CHCl_3$–MeOH, 100:1), 29–31 ($CHCl_3$–MeOH, 50:1), 32–40 ($CHCl_3$–MeOH, 20:1). The material from fractions 4 and 5 was combined and recrystallized to give euparin as yellow needles, wt 0·09 g, mp 119–120° (lit. mp 120–121° [16]), identical with an authentic sample [5] in mmp IR and NMR spectrum. Fractions 6–10 which showed one major spot on TLC were combined. Recrystallization from MeOH afforded acetylchapliatrin (**1c**), wt 1·5 g, mp 143°, $[\alpha]_{Hg}^{22}$ −53° (C 0·9, $CHCl_3$); CD curve $[\theta]_{263}$ −1290; $[\theta]_{240}$ 0, $[\theta]_{215}$ −21600 (last reading); IR bands at 1770, 1735, 1715 and 1650 cm^{-1}; UV strong end absorption at 220 nm; high resolution mass spectrum *m/e* (composition, %) 522 (M^+, $C_{26}H_{34}O_{11}$, 3·7), 480 ($C_{24}H_{32}O_{10}$, 9·1), 463 ($C_{24}H_{31}O_9$, 5·1), 462 ($C_{24}H_{30}O_9$, 7·1), 420 ($C_{22}H_{28}O_8$, 4·6), 402 ($C_{22}H_{26}O_7$, 4·8), 364 ($C_{19}H_{24}O_7$, 17·4), 323 ($C_{17}H_{23}O_6$, 13·4), 322 ($C_{17}H_{22}O_6$, 22), 304 ($C_{17}H_{20}O_5$, 13), 263 ($C_{15}H_{19}O_4$, 6·0), 262 ($C_{15}H_{18}O_4$, 8·5), 244 ($C_{15}H_{16}O_3$, 24·3), 141 ($C_7H_9O_3$, 29·3), 99 ($C_5H_7O_2$, 17·2). (Calcd. for $C_{26}H_{34}O_{11}$: C, 59·77; H, 6·55; O, 33·68. Found: C, 59·58; H, 6·76; O, 33·29).

Fractions 11–25 showed one major spot and were combined, wt 5 g. Rechromatography over 80 g of Si gel gave chapliatrin (**1a**) as a gum which was purified by preparative TLC on Si gel C_6H_6–EtOAc, 1:1), yield 3 g, identical in all respects with material from *L. chapmanii*. Acetylation (C_5H_5N–toluenesulfonic acid) furnished crystalline **1c**. Fractions 26–28 were combined and recrystallized from $CHCl_3$–C_6H_6 to give 3′,6-dimethoxy-4′,5,7-trihydroxyflavone, yield 0·02 g, mp 227–230° (lit. mp 227–228° [18]), identical in all respects (mmp, TLC, IR, NMR) with an authentic sample [21]. Combination of fractions 29–31 and recrystallization from methanol gave 0·04 g of 6-methoxy-4′,5,7-trihydroxyflavone (hispidulin), mp 292° (lit. mp 290° [17]), identical in all respects (mmp, TLC, IR, NMR) with an authentic sample.

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