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LASIOCARPIN A, B AND C, THREE NOVEL PHENOLIC TRIGLYCERIDES FROM *POPULUS LASIOCARPA*

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Key Word Index—*Populus lasiocarpa*; Salicaceae; bud excretion; phenolic triglycerides; 1,3-di-*p*-coumaryl-2-acetyl glycerol; 1-*p*-coumaryl-3-caffeyl-2-acetyl glycerol; 1,3-di-caffeyl-2-acetyl glycerol.

Abstract—The lipophilic excretion of winter buds of many species of *Populus* contains a variety of flavonoid aglycones. In *Populus lasiocarpa*, however, neither flavonoids nor free phenolic acids have been detected. Instead we found 3 novel phenolic triglycerides as major components of bud exudate in this species. Their structures have been shown by spectral and chemical evidence to be 1,3-di-*p*-coumaryl-2-acetyl glycerol, 1-*p*-coumaryl-3-caffeyl-2-acetyl glycerol, or its antipode, and 1,3-di-caffeyl-2-acetyl glycerol.

INTRODUCTION

Winter buds of many species in the genera *Alnus*, *Betula* (Betulaceae) [1], *Aesculus* (Hippocastanaceae) [2] and *Populus* (Salicaceae) [3] are covered with lipophilic material. We have previously reported that the excretions on dormant male flowers of *Alnus sieboldiana* and *A. pendula* are composed of various phenylpropane derivatives, such as β-phenylethyl cinnamate, flavonoids, stilbenes possessing antifungal properties, and rare natural diarylheptanoids [4–7]. In the genera *Alnus* and *Betula* the existence of species-specific flavonoid patterns in bud exudates has recently been shown [1]. The same is true for *Populus*, where among a variety of flavonoid aglycones a unique C-3 acetylated flavonol has been found [8]. These phenolics, which mostly occur together with terpenoids, are excreted by glandular trichomes in *Aesculus* and in Betulaceae, and by a glandular epithelium in *Populus* [cf. 9].

As a part of our screening program for flavonoids in the genus *Populus*, and as an extension of the chemotaxonomic investigations based on phenylpropane derivatives, we have studied the chemical constituents of the lipophilic coat on the winter buds of *Populus lasiocarpa* Oliv. The present paper reports on the isolation, and elucidation of structures of the three novel diacyl monoacetins **1**, **2** and **3**, for which we propose the names lasiocarpins A, B and C.

RESULTS

A preliminary examination of the extract of vegetative and reproductive buds by TLC indicated the presence of 3 major components. These were separated by column chromatography on silica gel and purified by preparative-TLC using benzene, ethyl acetate and methanol to furnish 3 pure substances, named lasiocarpins.

Lasiocarpin A (**1**)

The structure of lasiocarpin A was previously suggested to be 1,3-dicoumaryl-2-acetyl glycerol on the basis of alkaline hydrolysis, the lack of optical rotation and optical rotatory dispersion, and the similarity of the PMR signal pattern of the methylene and methine protons to those of triacetin and tristearin [10]. To determine the exact position of the acetyl group, the compound was treated with pancreatic lipase in the presence of $CaCl_2$ and bile salt solution [11]. However, this method produced no hydrolysis of **1**. The correctness of the structure of lasiocarpin A was deduced from acid-catalysed partial hydrolysis of lasiocarpin A diMe ether **4**, derived from **1** by treatment with dimethyl sulphate. The compound **4** was hydrolysed with 0.5 N HCl to give 2-desacetyl lasiocarpin A diMe ether **9**, whose IR, PMR (Table 1) and MS showed no signal corresponding to an acetyl group. Acetylation of the desacetyl derivative **9** with acetic anhydride regenerated **5**. From the above chemical evidence the structure of lasiocarpin A is confirmed as **1**.

This structure is further supported by the synthesis of tetrahydrolasiocarpin A diMe ether **12**. Glycerol was treated with *p*-methoxy dihydrocinnamoyl chloride in pyridine to give 1,3-diacyl glyceride in good yield which, on acetylation with acetic anhydride, furnished 1,3-diacyl monoacetin, whose spectral and chromatographic behaviour were identical with those of compound **12**.

Lasiocarpin B (**2**)

The molecular formula $C_{23}H_{22}O_9$ was advanced for lasiocarpin B on the basis of elemental analysis and MS data. The UV and IR spectra of the compound closely resembled those of **1**. The PMR spectrum (Table 1) showed 22 protons: one aliphatic acetate (2.06 ppm), one proton bearing acetyl group (5.38 ppm), and four AB-type protons at 4.32 and 4.48 ppm, assignable to two OCH_2 groups bearing one methine, and the complex signals for the aromatic regions. The presence of *p*-hydroxycinnamate and 3,4-dihydroxycinnamate groups was indicated by the presence of intense peaks at *m/e* 147

Table 1. PMR data* of lasiocarpins

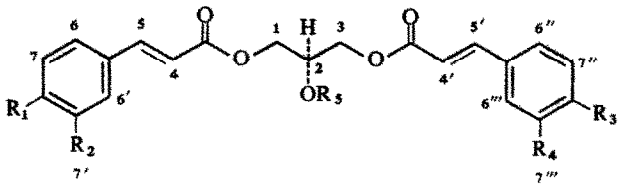
Compounds	2	3	4	5
2-OAc	2.06*s*	2.04*s*	2.10*s*	2.15*s*
2-H	5.38*m*	5.38*m*	5.40*m*	5.43*m*
1,3-H	4.32*dd*, *J* = 12, 6 4.48*dd*, *J* = 12, 4	4.23*dd*, *J* = 11, 6 4.47*dd*, *J* = 11, 4	4.36*dd*, *J* = 12, 6 4.43*dd*, *J* = 12, 4	4.30*dd*, *J* = 10, 7 4.57*dd*, *J* = 10, 4
4-H	6.28*d*, *J* = 16	6.28*d*, *J* = 16	6.28*d*, *J* = 16	6.33*d*, *J* = 16
4′-H	6.35*d*, *J* = 16			
5-H	7.57*d*, *J* = 16	7.54*d*, *J* = 16	7.65*d*, *J* = 16	7.69*d*, *J* = 16
5′-H	7.64*d*, *J* = 16			
6-H	7.03*bd*, *J* = 8	7.02*dd*, *J* = 8, 2		7.13*dd*, *J* = 9, 2
6′-H	7.15*bs*	7.15*d*, *J* = 2		7.06*s*
6″-H	7.51*d*, *J* = 8	7.02*dd*, *J* = 8, 2	7.46*d*, *J* = 9	7.48*d*, *J* = 9
6‴-H		7.15*d*, *J* = 2		
7-H	6.85*d*, *J* = 8	6.84*d*, *J* = 8		6.85*d*, *J* = 9
7′-H	—	—		—
7″-H	6.87*d*, *J* = 8	6.84*d*, *J* = 8	6.87*d*, *J* = 9	6.89*d*, *J* = 9
7‴-H		—		
Ar-OMe	—	—	3.83*s*	3.86*s*
Ar-OAc	—	—	—	3.90*s*

*The spectra of the compounds (2,3) were run in CD_3COCD_3 and those of the compounds (4–8) in $CDCl_3$. Chemical doublet †The signals of 2-H and 1,3-H were overlapped.

and 163 in the MS and by the following chemical reaction. Methylation of **2** gave the viscous Me ether **5**, indicating the presence of 3 phenolic OH groups. Hydrogenation of **5** in the presence of Pd-C gave a tetrahydroderivative **14**, indicating two double bonds. Treatment of **2** with acetic anhydride in pyridine produced the tetraacetate **7**. Alkaline hydrolysis of **5** gave acetic acid, glycerol and a mixture of aromatic acids. The latter was methylated with diazomethane to produce equimolar amounts of Me *p*-methoxy cinnamate and Me 3,4-dimethoxy cinnamate, which were separated by preparative-TLC and compared with authentic specimens. The above evidence showed that lasiocarpin B is an asymmetrical triglyceride with acetic, *p*-hydroxycinnamic and 3,4-dihydroxy cinnamic acids. The location of the acetyl group at C-2 was confirmed by partial acid hydrolysis. Treatment of **5** with dilute HCl gave 2-desacetyl lasiocarpin triMe ether **10**, which showed no signal corresponding to an acetyl group in PMR (Table 1), IR and MS, indicating the elimination of the acetyl group from C-2 position of compound **5**. Thus, the structure of lasiocarpin B was established as 1-*p*-coumaryl-3-caffeyl-2-acetyl glycerol or its antipode.

Lasiocarpin C (**3**)

The third major component of the excretion crystallized in acetone, mp 160–162°, $C_{23}H_{22}O_{10}$. The UV and IR spectra of this compound indicated the analogous 1,3-diacyl monoacetin system as described above. The PMR signal pattern of the aromatic region (Table 1) and prominent peaks of the MS showed again the



(1) $R_1 = R_3 = OH$, $R_2 = R_4 = H$, $R_5 = Ac$
(2) $R_1 = R_2 = R_3 = OH$, $R_4 = H$, $R_5 = Ac$
(3) $R_1 = R_2 = R_3 = R_4 = OH$, $R_5 = Ac$
(4) $R_1 = R_3 = OMe$, $R_2 = R_4 = H$, $R_5 = Ac$
(5) $R_1 = R_2 = R_3 = OMe$, $R_4 = H$, $R_5 = Ac$
(6) $R_1 = R_2 = R_3 = R_4 = OMe$, $R_5 = Ac$
(7) $R_1 = R_2 = R_3 = OAc$, $R_4 = H$, $R_5 = Ac$
(8) $R_1 = R_2 = R_3 = R_4 = OAc$, $R_5 = Ac$
(9) $R_1 = R_3 = OMe$, $R_2 = R_4 = H$, $R_5 = H$
(10) $R_1 = R_2 = R_3 = OMe$, $R_4 = R_5 = H$
(11) $R_1 = R_2 = R_3 = R_4 = OMe$, $R_5 = H$

and their derivatives

6	7	8	9	10	11
2.15*s*	2.13*s*	2.10*s*	—	—	—
5.46*m*	5.46*m*	5.31*s*			
4.30*dd*, *J* = 12, 6	4.35*dd*, *J* = 12, 6	4.30*dd*, *J* = 12, 6	4.33*bs*†	4.30*m*†	4.35*m*†
4.61*dd*, *J* = 12, 4	4.48*dd*, *J* = 12, 4	4.52*dd*, *J* = 12, 4			
6.38*d*, *J* = 16	6.43*d*, *J* = 16	6.36*d*, *J* = 16	6.30*d*, *J* = 16	6.26*d*, *J* = 16	6.31*d*, *J* = 16
7.75*d*, *J* = 16	7.70 or 7.75*d*, *J* = 16	7.66*d*, *J* = 16	7.69*d*, *J* = 16	7.43*d*, *J* = 16	7.66*d*, *J* = 16
	7.70 or 7.75*d*, *J* = 16				
7.20*dd*, *J* = 8, 1	7.40*bs*		7.48*d*, *J* = 8	7.02*dd*, *J* = 8, 2	7.08*s*
7.15*bs*				7.00*bs*	7.03*s*
7.20*dd*, *J* = 8, 1	7.59*d*, *J* = 9	7.36*bs*		7.43*d*, *J* = 8	7.08*dd*, *J* = 8, 2
7.15*bs*					7.03*s*
6.90*bd*, *J* = 8	7.40*bs*			6.79*d*, *J* = 8	6.80*bd*, *J* = 8
—	—	—	6.87*d*, *J* = 8	—	—
6.90*bd*, *J* = 8	7.15*d*, *J* = 9	7.36*bs*		6.84*d*, *J* = 8	6.80*bd*, *J* = 8
—	—	—		—	—
3.98*s*			3.82*s*	3.80*s*	3.93*s*
				3.90*s*	
—	2.35*s*	2.33*s*			

shifts in ppm. Signal multiplicity *s* = singlet, *d* = doublet, *dd* = double doublet, *bs* = broad singlet, *bd* = broad

presence of caffeic and acetic acids. This was proved by the following reactions. Acetylation of **3** gave the tetraacetyl derivative **8**. Methylation of **3** afforded the tetraMe ether **6**, which on alkaline hydrolysis gave caffeic acid, acetic acid and glycerol. The location of the acetyl group at C-2 of glycerol was supported by partial hydrolysis of **6**, as described above. Thus, the structure of lasiocarpin C was confirmed as 1,3-di-caffeyl-2-acetyl glycerol **3**. This structure was further supported by the synthesis of tetrahydrolasiocarpin C tetraMe ether **15** (see Experimental).

DISCUSSION

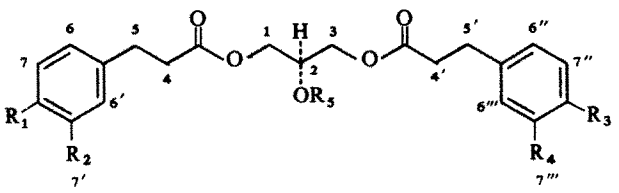
Acyl triglycerides are normal constituents of living organisms when composed with fatty acids. However, there are no examples of the isolation of triglycerides composed of aromatic acids. The occurrence of diacyl monoacetins is restricted to a small group of higher plants [12, 13] and an insect [14]. In these cases, the acetyl group is located at position C-3 of glycerol, and the other acyl groups are higher fatty acids. Thus the present phenolic triglycerides are rather simple but highly interesting structures, and lasiocarpins A, B and C are the first members of a new group of natural products.

Lasiocarpins are not found in the stem bark just beneath the buds. They are synthesized in the glandular epithelium of the scales like the flavonoid aglycones. In all the bud excretions examined hitherto [1–7] only one flavonoid with an acetyl group has been detected, 3-acetyl pinobanksin [8]. Simpler phenolics on the other hand occur in the exudation of *Populus balsamifera* [15]: acetophenone, *p*-hydroxy benzoic acid, 2,3-dihydroxy benzoic acid, cinnamic acid and the phenyl

Table 2. PMR data* of hydrogenated lasiocarpins and their derivatives

Compounds	12	13	14	15	16
2-OAc	2.10*s*	—	2.10*s*	2.05*s*	—
2-H	5.23*m*	4.10*bs*†	5.18*m*	5.23*m*	4.06*bs*†
1, 3-H	4.10*dd*, *J* = 12, 6		4.04*dd*, *J* = 12, 6	4.10*dd*, *J* = 12, 6	
	4.36*dd*, *J* = 12, 4		4.29*dd*, *J* = 12, 4	4.43*dd*, *J* = 12, 4	
4-H					
5-H	2.80*m*	2.80*m*	2.68*m*	2.75*m*	2.75*m*
6-H			6.71*bs*		
6′-H					
6″-H			7.09*d*, *J* = 8		
6‴-H	6.88*d*, *J* = 9	6.89*d*, *J* = 8		6.76*s*	6.88*bs*
7-H			6.71*bs*		
7′-H					
7″-H	7.03*d*, *J* = 9	7.12*d*, *J* = 9	—	—	—
7‴-H			6.78*d*, *J* = 8	6.76*s*	6.88*bs*
Ar-OMe	3.90*s*	3.81*s*	3.76*s*	3.90*s*	3.80*s*
			3.86*s*	3.92*s*	3.83*s*

*The spectra of the compounds were run in $CDCl_3$. †The signals of 2-H and 1,3-H were overlapped.



(12) $R_1 = R_3 = OMe$, $R_2 = R_4 = H$, $R_5 = Ac$
(13) $R_1 = R_3 = OMe$, $R_2 = R_4 = R_5 = H$
(14) $R_1 = R_2 = R_3 = OMe$, $R_5 = Ac$
(15) $R_1 = R_2 = R_3 = R_4 = OMe$, $R_5 = Ac$
(16) $R_1 = R_2 = R_3 = R_4 = OMe$, $R_5 = H$

ethyl ester of the latter. These compounds are not encountered in *P. lasiocarpa*, nor are there ferulic acid, isoferulic acid and chlorogenic acid which recently have been found in several species [16]. However, we observed compounds with similar behaviour as our lasiocarpins in other species of *Populus*, especially of the tribes Leuce and Leucoides. Investigations on this subject are in progress.

EXPERIMENTAL

Mps are uncorr. UV spectra were in 95% EtOH; IR and optical rotations were in $CHCl_3$ unless otherwise stated. PMR spectra were run in $CDCl_3$ or CD_3COCD_3 at 90 MHz. MS were recorded using a direct inlet system at 70 eV. ORD curves were measured in MeOH. TLC was done with Si gel G using C_6H_6–EtOAc–MeOH (10:4:1); spots were detected with UV light.

Isolation of lasiocarpin A, B and C. The winter buds (*ca* 4.2 kg) (Lot. Botanical Garden of University of Heidelberg) collected in March were percolated at room temp. with Me_2CO to exhaustion. After removal of the solvent at red. pres. at 40° the residue (7.32 g) was partitioned between 150 ml EtOAc and 50 ml H_2O. The EtOAc layer was dried (Na_2SO_4) and evapd at red. pres. The residue (4.32 g) showed 3 major spots by TLC. The residue (3.86 g) was directly chromatographed on Si gel using a C_6H_6–EtOAc–MeOH gradient. On crystallization from dil. HOAc, fractions 5–8 (500 mg), gave lasiocarpin A (210 mg), mp 121–122°. Fractions 10–12 (1.82 g) were rechromatographed on Si gel using the same solvent as above to give lasiocarpin A (200 mg) and lasiocarpin B (1.52 g). The colour of the latter compound gradually turned from pale yellow to brown on TLC. Fractions (17–20) were dissolved in Me_2CO to deposit a white powder, which was washed with hot Me_2CO several times to give pure lasiocarpin C (1.2 g).

Methylation of lasiocarpin A. **1** (200 mg) in dry Me_2CO (25 ml) was methylated with $(Me)_2SO_4$ (1 ml) in the presence of dry K_2CO_3 (3 g). Usual work up gave viscous lasiocarpin A diMe ether **4** (188 mg). $C_{25}H_{26}O_8$ (M^+ 454); UV λ_{max}: 313 nm (log ε, 4.03); IR ν_{max}: 1740, 1720, 825 cm^{-1}. PMR (Table 1).

Partial hydrolysis of lasiocarpin A diMe ether. **4** (52 mg) in Me_2CO was hydrolysed with 0.5N HCl under reflux for 24 hr. After evaporation of solvent, the residue was extracted with Et_2O to give a viscous oil, which was purified by prep-TLC and yielded 30 mg of 1,3-diacyl glycerol **9**, $C_{23}H_{24}O_7$ (M^+ 412). UV λ_{max}: 311 nm (log ε, 4.10); IR ν_{max}: 3500, 1720, 1635, 1260 cm^{-1}. PMR (Table 1).

Lasiocarpin B. Yellow viscous oil, $C_{23}H_{22}O_9$ (M^+ 442); $[\alpha]_D \pm 0.0°$; ORD no dispersion; $FeCl_3$-test green; UV λ_{max}: 223 (log ε, 3.85), 235 (3.70), 300 *sh* (3.91), 322 (4.01) nm; UV λ_{max}^{NaOH}: 374 nm (4.55). IR ν_{max}: 3350, 1740, 1710, 1615, 1605, 1590, 1515, 1270, 1170, 980, 830 cm^{-1}. PMR (Table 1). Analysis: C, 62.46%, H, 4.98%; calc. for $C_{23}H_{22}O_9$: C, 62.44%, H, 5.01%.

Lasiocarpin C. Colourless crystals, mp 160–162°, $C_{23}H_{22}O_{10}$ (M^+ 458); $[\alpha]_D \pm 0.0°$; ORD no dispersion; $FeCl_3$-test green; UV λ_{max}: 220 (log ε, 4.43), 237 (4.25), 248 (4.28), 302 *sh* (4.25), 336 (4.56) nm, UV λ_{max}^{NaOH}: 268 (4.23), 314 (4.09), 388 (4.63) nm. IR ν_{max}: 3440, 3210, 1745, 1670, 1635, 1610, 1530, 1240, 1115, 860, 825 cm^{-1}. PMR (Table 1). Analysis. C, 60.24%, H, 4.81%; calc. for $C_{23}H_{22}O_{10}$: C, 60.26%, H, 4.84%.

Acetylation of lasiocarpin B. **2** (115 mg) was acetylated with Ac_2O–Py at room temp. for 3 days. Work up in the usual manner gave a yellow oil, which was purified by prep-TLC to produce lasiocarpin B triacetate **7** as a colourless oil (98 mg), $C_{29}H_{28}O_{12}$ (M^+ 568); $[\alpha]_D \pm 0.0°$. UV λ_{max}: 219 (log ε, 3.77), 226 *sh* (3.68), 284 (3.95), 306 *sh* (3.72) nm; IR ν_{max}: 1765, 1740, 1640, 1505, 1240, 1170, 1010, 980, 830 cm^{-1}. PMR (Table 1).

Methylation of lasiocarpin B. **2** (1.32 g) in dry Me_2CO (50 ml) was treated with Me_2SO_4 (3 ml) in the presence of dry K_2CO_3 (10 g) at 60° for 18 hr. Excess K_2CO_3 was filtered off and the filtrate was treated as usual to give a pale yellow viscous oil (1.29 g), which was purified by prep-TLC to give lasiocarpin B triMe ether **5** as a colourless oil, $C_{26}H_{28}O_9$ (M^+ 484), $[\alpha]_D \pm 0.0°$; UV λ_{max}: 221 (log ε, 3.54), 233 (3.49), 300 *sh* (3.70), 317 (3.78) nm; IR ν_{max}: 1750, 1720, 1635, 1605, 1520, 1260, 1160, 1030, 830 cm^{-1}. PMR (Table 1). Analysis: C, 64.49%, H, 5.88%; calc. for $C_{26}H_{28}O_9$: C, 64.45%, H, 6.83%.

Hydrogenation of lasiocarpin B triMe ether. **5** (108 mg) in MeOH was hydrogenated in the presence of Pd-C. Uptake of H_2 ceased after 2 mol had been absorbed. The filtered soln was taken to dryness *in vacuo* and the residue purified by prep-TLC to give tetrahydrolasiocarpin B trimethylether **14** (94 mg) as colourless oil, $C_{26}H_{32}O_9$ (M^+ 488). $[\alpha]_D \pm 0.0°$; UV λ_{max}: 227 log ε, 3.55), 285 (3.50) nm; IR ν_{max}: 1740, 1605, 1590, 1515, 1250, 1160, 1025, 825, 805, 760 cm^{-1}. PMR (Table 2).

Alkaline hydrolysis of lasiocarpin B triMe ether. **5** (151 mg) was treated with 5% KOH–MeOH under reflux at 75° for 2 hr. After evaporation of solvent, the reaction mixture was acidified with N HCl (4 ml) and then extracted with Et_2O. The Et_2O extract was dried and removal of solvent gave an acid mixture, in which HOAc was identified by GLC (R_t and co-injection). The mixture (105 mg) was methylated with CH_2N_2 and yielded equimolar proportions of two Me ethers (GLC and TLC). The mixture was purified by prep-TLC to give Me *p*-methoxycinnamate (25 mg) and Me 3,4-dimethoxycinnamate (30 mg), identical with authentic specimens (UV, IR, PMR). The aq. layer was concd to a small vol. and extracted with EtOAc (10 ml). Removal of solvent *in vacuo* gave a viscous oil (17 mg), whose IR and PMR (D_2O) spectra were identical to those of glycerol.

Partial hydrolysis of lasiocarpin B triMe ether. **5** (120 mg) in Me_2CO was treated with 0.5N HCl under reflux for 23 hr. After removal of solvent, the reaction mixture was extracted with Et_2O. Usual work-up gave a viscous oil, purified by prep-TLC to afford 1,3-diacyl glycerol **10** (87 mg), $C_{24}H_{26}O_8$ (M^+ 442). UV λ_{max}: 233 (log ε, 3.52), 295 *sh* (3.63), 315 (3.68) nm; IR ν_{max}: 3520, 1720, 1640, 1610, 1520, 1270, 1170, 990, 835, 765 cm^{-1}. PMR (Table 1).

Acetylation of 2-desacetyl lasiocarpin B triMe ether. **10** (57 mg) was acetylated with Ac_2O–Py (1 ml) at room temp. for 18 hr to give a triglyceride (53 mg), whose spectral and chromatographic behaviour was identical to that of lasiocarpin triMe ether **5**. As described in the above paragraph, lasiocarpin C (520 mg) and (250 mg) was treated with Me_2SO_4 and with Ac_2O, respectively, to give a tetraMe ether **6** (470 mg) and a tetraacetate

8 (220 mg). Lasiocarpin C tetraMe ether **6**, $C_{27}H_{30}O_{10}$ (M^+ + 1, 515, base), $[\alpha]_D$ ± 0.0°; UV λ_{max}: 219 (log ε, 4.36), 243 (4.34), 296 *sh* (4.36), 330 (4.38) nm; IR ν_{max}: 1750, 1710, 1635, 1600, 1515, 1260, 1020, 845, 810, 680 cm^{-1}. PMR (Table 1). Analysis: C, 63.08%, H, 5.84%; calc. for $C_{27}H_{30}O_{10}$: C, 63.03%, H, 5.88%. Lasiocarpin C tetraacetate **8**. $C_{31}H_{30}O_{14}$ (M^+ 626). $[\alpha]_D$ ± 0.0°; UV λ_{max}: 220 (log ε, 3.45), 226 *sh* (3.45), 282 (3.96) nm; IR ν_{max}: 1770, 1750, 1720, 1640, 1505, 1210, 1180, 1010, 905, 835, 755 cm^{-1}. PMR (Table 1).

Tetrahydrolasiocarpin C tetraMe ether. An EtOH soln of **6** was hydrogenated in the presence of prereduced Pd-C. The catalyst was filtered off and the solvent evapd to give viscous material, which was purified by prep-TLC to give the tetrahydro-derivative **15**, $C_{27}H_{34}O_{10}$ (M^+ 518). UV λ_{max}: 230 (log ε, 4.24), 280 (3.77), 287 *sh* (3.67) nm; IR ν_{max}: 1740, 1610, 1595, 1520, 1265, 1240, 1180, 1030, 810, 765 cm^{-1}. PMR (Table 2).

2-Desacetyl lasiocarpin C tetraMe ether **6** (67 mg) was hydrolysed under the same conditions described for the partial hydrolysis of compound **5**, to give 2-desacetyl lasiocarpin C tetraMe ether **11**, $C_{25}H_{28}O_9$ (M^+ 472). UV λ_{max}: 219 (log ε, 3.59), 240 (3.58), 297 (3.67), 326 (3.79) nm; IR ν_{max}: 3520, 1705, 1630, 1600, 1510, 1260, 1155, 1135, 1020, 845, 805, 750 cm^{-1}. PMR (Table 1).

Alkaline hydrolysis of lasiocarpin C tetraMe ether. **6** (100 mg) was treated with 5% KOH–MeOH under reflux at 80° for 3 hr. The solvent was evapd and the residue washed with Et_2O. The remaining powder was acidified with dil. HCl and extracted with Et_2O and dried. Removal of solvent gave a mixture of acids in which HOAc was identified as above. Evapn of HOAc, followed by recrystallization from Et_2O, gave white needles (58 mg), whose physical and spectral data were identical to those of 3,4-dimethoxy cinnamic acid. The aq. portion was concd and extracted with EtOAc. Evapn of solvent gave a viscous substance (18 mg), whose spectral data were identical to those of glycerol.

Synthesis of tetrahydrolasiocarpin A diMe ether. To anhydrous glycerol (580 mg) in dry Py (10 ml) and $CHCl_3$ (10 ml), *p*-methoxy dihydrocinnamoyl chloride (640 mg) was added at 0°, and the mixture then refluxed at 95° for 9 hr. The reaction product, after removal of solvent, was diluted with H_2O and extracted with Et_2O. The Et_2O layer was washed with dil. HCl and dried. Evapn of solvent gave crude diacyl glycerol **13** IR ν_{max}: 3500, 1725 cm^{-1}), which was acetylated as usual without purification. The product was chromatographed on Si gel using a C_6H_6–EtOAc gradient, to produce the triglyceride (433 mg), whose spectral and chromatographic characteristics were in accordance with those of tetrahydrolasiocarpin A diMe ether **12**.

Synthesis of tetrahedrolasiocarpin C tetraMe ether. Glycerol (255 mg) in Py (10 ml) and $CHCl_3$ (10 ml) was treated with 3,4-dimethoxydihydrocinnamoyl chloride (560 mg), derived from caffeic acid through 3 steps, as described above. The product was chromatographed on Si gel using a C_6H_6–EtOAc gradient to yield pure 1,3-diacyl glycerol **16** (437 mg). UV λ_{max}: 281 (log ε, 3.95), 287 *sh* (3.83) nm; IR ν_{max}: 3500, 1725, 1595, 1515, 1250, 1150, 1030, 855, 810, 765, 685 cm^{-1}. PMR (Table 1). Acetylation of the resultant 1,3-diacyl glycerol (150 mg) in the usual manner produced a triglyceride (135 mg), whose spectral and chromatographic properties were identical with those of authentic tetrahydrolasiocarpin C tetraMe ether **15**.

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