Pergamon 0031-9422(94)00569-9 Phytochemistry, Vol. 38, No. 1, pp. 199–204, 1995
Elsevier Science Ltd
Printed in Great Britain
0031 9422/95 $9.50 + 0.00

ABIETANE AND ICETEXANE DITERPENOIDS FROM *SALVIA CANDICANS**

JORGE CÁRDENAS and LYDIA RODRÍGUEZ-HAHN†

Instituto de Química de la Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México, D.F.

(*Received* 28 *April* 1994)

Key Word Index—*Salvia candicans*; Labiatae; abietanes; icetexanes; diterpenoids.

Abstract—Seven abietane and icetexane diterpenoids were isolated from the aerial parts of *Salvia candicans*. Three were identified as conacytone, icetexone and anastomosine. The other four were new diterpenes, whose structures were established by spectroscopic and chemical means. Two of them had an icetexane skeleton.

INTRODUCTION

During the course of the systematic study of Mexican *Salvia* species (subgenus *Calosphace*) [1], we have isolated a great number of *neo*-clerodane diterpenoids or diterpenes which could be derived biogenetically from a clerodane precursor [2]. Abietane diterpenoids have been isolated from *Salvia* species classified in section *Erytrosthachys*. The *Salvia* species belonging to section *Tomentellae* studied up to now contain abietane and icetexane diterpenoids [3, 4]. In this paper we report the diterpenoid content of *Salvia candicans* (section *Tomentellae*). In a previous communication we described the chemical constituents of *Salvia anastomosans* [5] recently classified in section *Tomentellae* which is morphologically related to *S. candicans* [6].

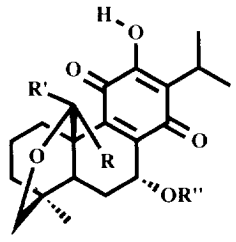
RESULTS AND DISCUSSION

Oleanolic and ursolic acids, conacytone (**1**) as the 7-*O*-methyl ether (**1a**), icetexone (**7**), anastomosine (**8**) and four new diterpenoids were isolated from the acetone extract of the aerial parts of a population of *Salvia candicans*. The structure of 7-*O*-methyl conacytone (**1a**) was confirmed by oxidation with Jones reagent to give **1b**. Compound **1b** had a molecular formula $C_{21}H_{26}O_6$ (MS) ($[M]^+$ at *m/z* 374). The IR spectrum of **1b** exhibited a band for a δ-lactone (1724 cm^{-1}). The ^1H NMR spectrum (Table 1) showed a singlet at δ4.22 (2H) which was assigned to the protons at C-19 and a singlet at δ3.45 (3H) for a methoxy group. Conacytone (**1**) had been previously isolated when no methanol was used in the separation process [7], therefore 7-*O*-methyl conacytone is an artifact which could be formed by the participation of the hydroxy group at C-20.

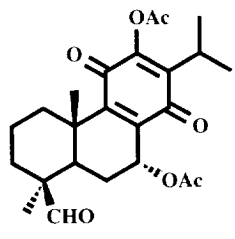
Compound **2** was isolated as an orange oil after acetylation of the mother liquors of the fractions eluted with hexane–ethyl acetate (19:1). It analysed for $C_{24}H_{30}O_7$ (CIMS). The IR spectrum revealed bands for an aldehyde group (1719, 2721 cm^{-1}), enolic acetate (1772 cm^{-1}), ester group (1739 cm^{-1}) and *p*-quinoid carbonyls (1667, 1610 cm^{-1}), no hydroxy bands were observed. The ^1H NMR spectrum (Table 1) showed signals for two acetate methyl groups (δ2.34, 2.07): one enolic and the other must be geminal to the proton ascribed to the signal at δ6.06 (1H, *dd*, $J = 3$, 2 Hz, H-7) in a pseudo equatorial orientation. The signals due to the isopropyl group attached to a *p*-quinone ring appeared at δ3.38, 1H, *septet*, $J = 7$ Hz, H-15; δ1.20 and 1.18, 3H each, *d*, Me-16 and Me-17. Two methyl singlets (3H each one) at δ1.02 and 1.13, and a singlet at δ9.71 (1H), were ascribed to two tertiary methyls and a formyl group bound to C-4 and C-10 in an abietane quinone skeleton. The chemical shift observed in the ^1H NMR for the aldehydic proton in **2** is at higher field ($\Delta\delta = -0.38$) than the one reported for nemorone and deacetylnemorone, abietane quinone diterpenes with a formyl group at C-10 isolated from *Salvia nemorosa* [8]. Hence the aldehyde group in **2** was at C-4. The ^{13}C NMR spectrum of **2** (Table 2) showed signals for the formyl carbon (δ204.3) and a fully substituted carbon at δ47.7, both signals were in agreement with those reported for abietane diterpenes with an aldehyde group attached to C-4 [9]. The orientation of the substituents at C-4 was deduced from the chemical shift due to C-5 in the ^{13}C NMR spectrum (δ46.9), which corresponds to an abietane with a formyl group in the axial position at C-4, taking into account the shielding effect on C-5 produced by the pseudo axial acetoxy group at C-7.

Compound **3** was obtained as an amorphous yellow solid mp 110–115°. It analysed for $C_{20}H_{26}O_6$ by mass spectrometry ($[M]^+$ at *m/z* 362). This product showed two spots in the normal TLC and four in a bidimensional TLC, which suggested that **3** was susceptible to equilibration in the acidic medium. Its IR spectrum had absorp-

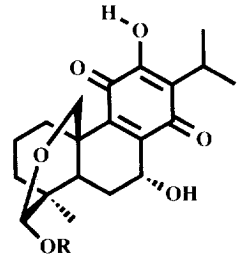
*Contribution No. 1253 from Instituto de Química, UNAM.
†Author to whom correspondence should be addressed.



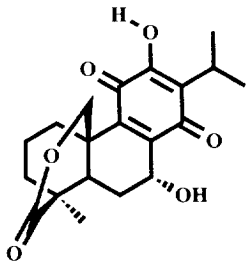
1 R=OH, R''=R=H
1a R=OH, R'=H, R''=Me
1b R, R'=O, R''=Me



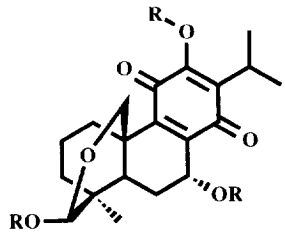
2



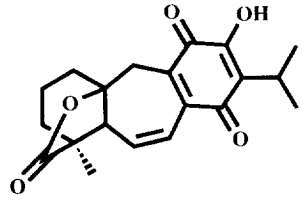
3a R=H
6 R=Me



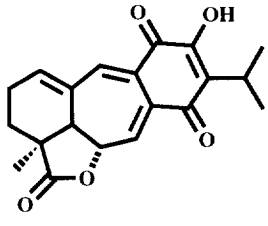
4



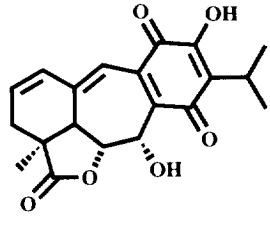
3b R=H
5 R=Ac



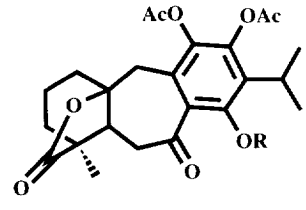
7



8



9



10 R=H
11 R=Ac

tions for hydroxy groups (3596, 3391 cm^{-1}) and *p*-quinoid carbonyls (1648, 1630, 1608 cm^{-1}). The ^1H NMR spectrum showed the characteristic signals for an isopropyl group attached to a hydroxy *p*-quinone ring. A singlet at δ 7.20 (exchangeable with D_2O) was ascribed to a chelated phenolic hydroxy group. The remaining spectrum showed duplicated signals for all the spin systems with a molar ratio 2:1. The signals at δ4.7–4.9 were ascribed to geminal protons to oxygenated functions, one of them to H-7 in an abietane quinoid diterpene and the other to an hemiacetalic proton (Table 1). Two methyl singlets were observed at δ1.03 and 0.95 (Me-18) (molar ratio 2:1). In addition two AB parts of ABX systems were observed at δ4.13 *d*, 3.87 *dd* and 4.41 *d*, 3.72 *dd*, both systems with a geminal coupling ($J = 12$ Hz) and a long range coupling ($J = 2$ Hz). The difference in chemical shift and the long range coupling is indicative of the same conformation in the A ring in both compounds. Product **3** is an isomer of conacytone **1**. Treatment of **3** with Jones reagent afforded deacetyl sesseine (**4**), whose ^1H NMR spectrum was compared with the spectrum of an authentic sample [10]. The stereochemistry at C-19 was proposed by the chemical shifts observed for the AB part of the ABX systems. The double doublet signals (δ3.87 and 3.72) were ascribed to both H-20 *pro-S* (see below). The signal at lower field was assigned to the most abundant isomer with the hydroxy group at C-19 in a 1–3 diaxial relationship with H-20 *pro-S*. Treatment of **3** with acetic anhydride in pyridine afforded the acetyl derivative **5**. Its IR spectrum showed bands for enolic acetate (1773 cm^{-1}), ester group (1744 cm^{-1}) and *p*-quinoid carbonyls (1665, 1615 cm^{-1}), no hydroxy bands were observed. The ^1H NMR spectrum exhibited the signals for only one compound with three acetate groups (δ2.35, 2.13 and 2.06). The signals assigned to H-7 and H-19 were downfield shifted to δ6.0 (*t*, $J = 3$ Hz) and 5.56 (*s*), respectively. The AB part of the ABX system appeared at δ4.56 (*d*, $J = 12$ Hz) and 3.78 (*dd*, $J = 12$, 2 Hz). Spin decoupling experiments led to the assignment of the diasterotopic protons at C-20 and confirm some other assignments.

Table 1. ^{1}H NMR data of compounds **1a–3b**, **5**, **6**, **9–11** (300 MHz, $CDCl_3$, TMS as int. standard)

H	1a	1b	2	3a	3b	5	6	9	10*	11†
1α						1.46 *tdd* (13, 6, 2)		6.51 *dd* (10, 3)		
1β						2.68 *td* (13, 6)	2.75 *dd* (13, 6)			
2α						1.62 *dt* (13, 6)		6.17 *ddd* (10, 6, 3)		
2β						2.54 *tt* (13, 6)				
3α						1.25 *td* (13, 6)		2.32 *dd* (16, 6)		
3β						2.13 *m*		2.42 *br d* (16)		
5						1.80 *br d* (13)		2.73 *d* (11)	0.78 *d* (12.8)	
6α						2.06 *m*			2.37 *d* (17.4)	
6β						1.91 *td* (13, 3)		4.44 *dd* (11, 8)	2.09 *dd* (17.4, 12.8)	
7	4.43 *dd* (3, 2)	4.40 *t* (3)	6.06 *dd* (3, 2)			6.00 *t* (3)	4.70 *t* (3)	5.31 *d* (8)	—	—
15	3.21 (7)	3.17 (7)	3.12 (7)	3.17 (7)	3.17 (7)	3.13 (7)	3.14 (7)	3.27 (7)	3.44 (7)	3.12 (7)
16	1.25 (7)	1.21 *d* (7)	1.02 *d* (7)	1.22 *d* (7)	1.22 *d* (7)	1.20 *d* (7)	1.21 *d* (7)	1.24 *d* (7)	1.49 *d* (7)	1.30 *d* (7)
17	1.22 *d* (7)	1.19 *d* (7)	1.18 *d* (7)	1.20 *d* (7)	1.20 *d* (7)	1.18 *d* (7)	1.20 *d* (7)	1.24 *d* (7)	1.52 *d* (7)	1.20 *d* (7)
18	0.80 *s*	0.99 *s*	1.02 *s*	1.03 *s*	0.95 *s*	0.80 *s*	0.94 *s*	1.30 *s*	0.76 *s*	1.15 *s*
19	3.86 *dd* (11, 2.4) 3.32*d* (11)	4.22 *s*	9.71 *s*			5.56 *s*	4.22 *s*			
20	5.61 *d* (2.6)	—	1.13 *s*	4.13 *d* (12) 3.87 *dd* (12, 2)	4.41 *d* (12) 3.72 *dd* (12, 2)	4.56 *d* (12) 3.78 *dd* (12, 2)	4.10 *d* (11) 3.63 *dd* (11, 2)	6.64 *s*	3.06 *d* (14) 2.52 *d* (14)	3.15 *d* (14) 2.77 *d* (14)
OH	7.08 *s*	7.30 *s*		7.20 *s*	7.20 *s*		7.18 *s* 2.66 *s*	7.14 *s*	13.72 *s*	
OMe	3.45 *s*	3.45 *s*					3.26 *s*			
OAc			2.07 *s* 2.34 *s*			2.35 *s* 2.13 *s* 2.06 *s*			1.72 *s*	2.31 *s* 2.25 *s*

Coupling constants in Hz are in parentheses. Chemical shifts are in δ values.
*Run in C_6D_6 solution.
†Run at 80 MHz.

Irradiation of the double doublet at δ3.78 simplified the signal at δ1.46 (H-1α). The saturation at δ1.46 simplified the resonances at δ2.68, 2.54, 1.62 and 3.78 which were assigned to H-1β, H-2β, H-2α and H-20 *pro-S*, respectively. On the other hand decoupling of the signal at δ6.0 led to the assignment of H-6β (δ1.91, *td*, $J = 13, 4$ Hz) and H-6α (2.06, *m*).

Product **6** was isolated as yellow crystals, mp 199–200°. The IR spectrum revealed hydroxy bands (3583 and 3390 cm^{-1}) and *p*-quinoid carbonyls (1648, 1630 cm^{-1}). The ^{1}H NMR spectrum showed the signals for only one product. The proton at δ4.22 (*s*, 1H) and the methoxy group at δ3.26 (*s*, 3H) were bound to the ketalic C-19. The H_2-20 signal was observed as the AB part of an ABX system at δ4.10 (*d*, $J = 11$ Hz) and 3.63 (*dd*, $J = 11$, 2 Hz). Compound **6** is the C-19 methyl ketal of **3**. Treatment of **3** with methanol and TFA afforded **6** quantitatively.

The long range coupling of H-20 *pro-S* with H-1α in the ^{1}H NMR spectra of compounds **3a**, **3b**, **5** and **6** is only possible if the ethereal oxygen between C-19 and C-20 is oriented towards C-2. The analysis of the chemical shifts in the ^{1}H NMR spectrum for the protons at C-20 led to the assignments of the relative stereochemistry as shown in the structures.

Product **9** was isolated as an amorphous orange solid. Its IR spectrum showed bands for hydroxy groups (3579, 3412 cm^{-1}), γ-lactone (1778 cm^{-1}), *p*-quinoid carbonyls

Table 2. ^{13}C NMR spectral data of compounds **2**, **9** and **10** in $CDCl_3$

C	2	9	10
1	35.0 *t*	131.2 *d*	35.5 *t*
2	18.6 *t*	128.2 *d*	19.4 *t*
3	33.7 *t*	30.7 *t*	34.3 *t*
4	47.7 *s*	40.1 *s*	47.5 *s*
5	46.9 *d*	44.7 *d*	49.9 *d*
6	24.4 *t*	80.9 *d*	40.8 *t*
7	63.7 *d*	74.3 *d*	205.6 *s*
8	139.4 *s*	138.8 *s*	129.9 *s*
9	*	139.9 *s*	134.1 *s*
10	39.2 *s*	131.2 *s*	84.3 *s*
11	*	183.9 *s*	126.7 *s*
12	151.5 *s*	150.1 *s*	146.6 *s*
13	137.9 *s*	127.3 *s*	117.4 *s*
14	*	187.9 *s*	161.8 *s*
15	25.2 *d*	24.6 *d*	26.3 *d*
16	20.2 *q*	19.8 *q*	20.1 *q*
17	20.2 *q*	19.7 *q*	19.9 *q*
18	23.9 *q*	23.3 *q*	17.0 *q*
19	204.3 *d*	179.1 *s*	178.2 *s*
20	17.9 *q*	117.2 *d*	32.9 *t*
MeCO	169.4 *s*		168.3 *s*
	168.3 *s*		167.5 *s*
MeCO	21.0 *q*		20.5 *q*
	20.4 *q*		20.3 *q*

*Unobserved signals.

Multiplicities were obtained by DEPT experiments and are in parentheses.

(1655, 1628 cm^{-1}) and a double bond (1570 cm^{-1}). The ^{13}C NMR spectrum (Table 2) was consistent with the functional groups described in the IR, furthermore four sp^2 carbons and two oxygenated sp^3 carbons were observed. The ^{13}C NMR and the IR spectra were in accordance with a $C_{20}H_{20}O_6$ molecular formula. The ^1H NMR spectrum (Table 1) showed the characteristic signals due to an isopropyl group in a hydroxy *p*-quinone ring and a singlet (3H) at δ1.30 assigned to the tertiary Me-18. The spectrum also showed two vinylic protons at δ6.51 (*dd*, J = 10, 3 Hz, H-1) and 6.17 (*ddd*, J = 10, 6, 3 Hz, H-2) in a six membered ring, coupled with protons of a methylene at δ2.42 (*br d*, J = 16 Hz, H-3β) and 2.32 (*dd*, J = 16, 6 Hz, H-3α). A double doublet at δ4.44 (J = 11, 8 Hz) was ascribed to the proton bound to the γ-lactone closure, H-6, which is coupled to the proton responsible for the doublet at δ2.73 (J = 11 Hz, H-5) and to the signal at δ5.31 (*d*, J = 8 Hz) which was, therefore, attributed to H-7. The ^1H COSY spectrum showed a correlation between H-5 and a singlet at δ6.64 assigned to H-20, thus H-5 must be axially oriented [11]. The coupling constant of 11 Hz indicated an antiperiplanar relationship between H-5 and H-6, hence the γ-lactone closure must be pseudo equatorial. The coupling constant of 8 Hz is adequate for a dihedral angle H-6β–C-6–C-7–H-7$\beta \approx 0°$ in a boat conformation of ring B with the hydroxy group at C-7 α-oriented. The chemical shift observed for the γ-lactone carbonyl in the ^{13}C NMR spectrum at δ179.1 is similar to that found in anastomosine (**8**), an icetexane diterpene with a *trans*-19,6-olide function [5].

The fraction of the chromatography eluted with hexane–ethyl acetate (1:1), was an unresolved mixture. Treatment of this material with acetic anhydride–sodium acetate gave **10** after extensive chromatography. The same product was obtained under reductive acetylation of the mixture in the presence of Zn dust. Compound **10** had the molecular formula $C_{24}H_{28}O_8$ by mass spectrometry ($[M]^+$ at m/z 444). Its IR spectrum showed bands for phenolic acetates and γ-lactone carbonyl (1775 cm^{-1}), and chelated aryl ketone (1622 cm^{-1}). The ^1H NMR spectrum of **10** (C_6D_6, Table 1) revealed the presence of two aromatic acetoxy groups at δ1.72 and 1.71 (δ2.32 in $CDCl_3$), an isopropyl group bound to an aromatic ring and only one methyl singlet at δ0.76. A singlet at δ13.72 (1H, exchangeable with D_2O) was ascribed to a chelated phenol. An AB system was observed at δ3.06 and 2.52 (J = 14 Hz) attributed to the methylene protons at C-20 in an icetexane skeleton. Furthermore an ABX system at δ2.09 (*dd*, J = 17.4, 12.8 Hz, H-6β), 2.37 (*d*, J = 17.4 Hz, H-6α) and 0.78 (*d*, J = 12.8 Hz, H-5) was observed. The magnitude of the coupling constant of 17.4 Hz was due to a geminal coupling of a methylene bound to a ketone group. The ^{13}C NMR spectrum (Table 2) showed signals for an hexasubstituted benzene and a γ-lactone carbonyl (δ178.2). The singlet at δ84.3 was ascribed to the γ-lactone closure at C-10 and a ketone group at δ205.6 was in agreement with a chelated aryl ketone, therefore the carbonyl must be at C-7 and the phenolic group at C-14.

Acetylation of the same material with acetic anhydride in pyridine afforded compound **11**. Its IR spectrum showed bands for γ-lactone and phenolic acetates (1775 cm^{-1}) and aryl ketone (1691 cm^{-1}). The ^1H NMR spectrum of compound **11** (Table 1) was consistent with the acetyl derivative of **10**. It exhibited a new methyl acetate group at δ2.25 and the proton ascribed to a chelated phenol was not observed.

The isolation of icetexone (**7**), anastomosine (**8**) and the new icetexane diterpenoids **9** and the precursor of **10** is in accordance with the proposed botanical relationship of *S. candicans* with *S. anastomosans*.

EXPERIMENTAL

Mps: uncorr. MS were obtained at 70 eV by direct inlet, ^1H NMR (80, 200 or 300 MHz) using TMS as int. standard, ^{13}C NMR (50 or 75 MHz) $CDCl_3$ was taken as reference at 77 ppm. Plant material was collected at 10 km SE from Tehuacán (Puebla, México) and a voucher specimen (MEXU 531373) is deposited at the Herbarium of the Instituto de Biología, UNAM.

Isolation of the constituents of Salvia candicans. Dried aerial parts of *S. candicans* (5.2 kg) were extracted with Me_2CO (20 l) at room temp. for 1 week. The solvent was

removed under red. pres. During the evapn of the solvent a mixt. of ursolic and oleanolic acids was isolated by filtration (80.3 g). The extract (138.1 g) was partitioned between MeOH–H_2O (4:1) and hexane–C_6H_6 (1:1). The polar fr. (65.6 g) was subjected to vacuum chromatography over silica gel. Mixts of hexane–EtOAc of increasing polarity were used as eluents. From the frs eluted with hexane–EtOAc (19:1) and after exhaustive flash chromatography eluted with hexane–Me_2CO (49:1) 2 diterpenes were isolated, 7-*O*-methyl conacytone (**1a**) and **6**. The mother liquors of this fraction were subjected to acetylation to obtain **2**.

Icetexone (**7**) (153 mg) and anastomosine (**8**) (810 mg) were obtained from the frs eluted with hexane–EtOAc (9:1 and 4:1) and identified by comparison with authentic samples. Products **3** (292 mg) and **9** (7 mg) were obtained from the fractions eluted with hexane–EtOAc (7:3) after extensive flash chromatography. From the fractions eluted with hexane–EtOAc (1:1) an unresolved mixture (6.3 g) was obtained. The ^{1}H NMR spectrum of this mixture showed the absence of acetate groups.

7-O-*Methyl conacytone* (**1a**). Mp 213–215°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3596, 3395, 1640, 1150, 1110. ^{1}H NMR see Table 1. CIMS *m/z*: [M]$^+$ 376; EIMS *m/z* (rel. int.): 344 (43), 342 (20), 298 (100), 283 (25), 269 (35), 244 (30), 230 (50), 229 (46), 128 (30), 115 (40), 91 (30).

Compound **6**. Mp 199–200°; UV λ_{max}^{MeOH} (ε): 204 (13 300), 263 (7600), 402 (571). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3583, 3390, 1648, 1630, 1113, 1051. ^{1}H NMR see Table 1. MS *m/z* (rel. int.) 376 [M]$^+$ (0.1), 348 (2), 347 (10), 346 (52), 314 (8), 298 (8), 230 (18), 98 (25), 85 (30), 61 (30), 55 (70), 43 (100), 41 (68).

19-*Dihydro-deacetyl sesseine* (**3**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3596, 3391, 1648, 1630, 1608, 879. ^{1}H NMR see Table 1. EIMS *m/z* (rel. int.): 362 [M]$^+$ (9), 344 (9), 332 (25), 314 (45), 298 (35), 285 (80), 115 (37), 91 (60), 55 (67), 43 (100), 41 (86).

Compound **9**. $[\alpha]_D$ +772° ($CHCl_3$; *c* 0.036). UV λ_{max}^{MeOH} nm: (ε): 210 (11 550), 270 (10 900), 324 (4750), 438 (1350). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3579, 3412, 1778, 1655, 1628, 1570; ^{1}H NMR see Table 1; ^{13}C NMR see Table 2.

Preparation of compound **2**. The mother liquors of the fraction eluted with hexane–EtOAc (19:1) were treated with Ac_2O and pyridine. After usual work-up **2** was obtained as an orange oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2968, 2938, 2875, 2721, 1772, 1739, 1719, 1667, 1610. ^{1}H NMR see Table 1; ^{13}C NMR see Table 2. CIMS *m/z*: [M]$^+$ 430; EIMS *m/z* (rel. int.): 388 (2.2), 371 (2.4), 370 (2.4), 355 (1), 346 (10), 328 (21), 313 (5), 300 (9), 285 (5), 105 (4), 91 (6), 83 (10), 69 (6), 55 (11), 43 (100), 41 (11).

Preparation of compound **10**. A portion of the fraction (516 mg) eluted with hexane–EtOAc (1:1) was dissolved in Ac_2O (5 ml) and treated with recently dried NaOAc (618 mg) for 20 hr at room temp. After usual work-up 590 mg of a mixture was subjected to vacuum chromatography eluted with hexane–EtOAc (9:1). Compound **10** (8 mg) was isolated. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 1622. ^{1}H NMR, see Table 1; ^{13}C NMR see Table 2. EIMS *m/z* (rel. int.): 444 [M]$^+$ (1), 402 (12), 360 (29), 345 (1), 342 (1), 332 (0.5), 314 (6), 299 (2), 91 (4), 55 (7), 43 (100), 41 (4).

Preparation of compound **11**. A portion of the fraction (516 mg) eluted with hexane–EtOAc (1:1) in pyridine (3 ml) was treated with Ac_2O at room temp. for 14 hr. After usual work-up and vacuum chromatography compound **11** (13.6 mg) was isolated. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775, 1691, 1604. ^{1}H NMR see Table 1. EIMS *m/z* (rel. int.): 486 [M]$^+$ (not observed) 444 (0.1), 402 (0.1), 361 (0.1), 360 (0.3), 85 (2), 83 (4), 47 (3), 43 (100), 35 (5).

Oxidation of compound **1a**. Jones reagent was added dropwise to a soln of **1a** (63 mg) in Me_2CO (10 ml) at 0° during 40 min. After usual work-up and flash chromatography 14 mg of **1b** was obtained: mp 181–182° (EtOAc–hexane), $[\alpha]_D$ −91.56° (MeOH; *c* 0.164). UV λ_{max}^{MeOH} nm (ε): 203 (14 557), 262 (9730), 397 (921). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3382, 1724, 1638. ^{1}H NMR see Table 1. EIMS *m/z* (rel. int.): 374 [M]$^+$ (28), 359 (30), 346 (32), 342 (41), 331 (95), 314 (80), 227 (87), 185 (100), 165 (52), 141 (50), 129 (72), 115 (99), 91 (55), 77 (38), 55 (25), 41 (25).

Oxidation of compound **3**. Jones reagent was added dropwise to a soln of **3** (54 mg) in Me_2CO (10 ml) −10° during 6 min. After usual work-up and flash chromatography 12 mg of **4** was obtained.

Acetylation of compound **3**. A soln of **3** (30 mg) in pyridine (1 ml) and Ac_2O (1 ml) was left to stand for 14 hr at room temp. and worked-up as usual to give 20 mg of **5** as a yellow oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1773, 1744, 1665, 1615. ^{1}H NMR see Table 1. EIMS *m/z* (rel. int.): 488 [M]$^+$ ($C_{26}H_{32}O_9$; unobserved); 429 (0.7), 399 (0.1), 356 (3), 338 (2), 314 (8), 55 (3), 43 (100), 41 (4).

Preparation of compound **6**. A soln of **3** (30 mg) in MeOH (2 ml) was treated with TFA (1 drop) at room temp for 12 hr. Compound **6** was obtained quantitatively (TLC).

Acknowledgements—We are very grateful to Messrs Rubén Gaviño Gabriela Salcedo, Lilian Guevara, Carmen Márquez, Luis Velasco and Rocío Pafiso for technical assistance. We thank Dr T. P. Ramamoorthy (Botany Department, Instituto de Biología, UNAM) for botanical classification of the plant material.

REFERENCES

1. Epling, C. (1939) *Report. Spec. Nov. Regni. Veg. Beith.* **110**, 1.
2. Rodríguez-Hahn, L., Esquivel, B. and Cárdenas, J. (1992) *Trends Org. Chem.* **3**, 99.
3. Rodríguez-Hahn, L., Esquivel, B., Sánchez, A. A., Sánchez, C., Cárdenas, J. and Ramamoorthy, T. P. (1989) *Rev. Latinoam. Quím.* **20**, 105.
4. Rodríguez-Hahn, L., Esquivel, B., Cárdenas, J. and Ramamoorthy, T. P. (1992) in *Advances in Labiatae Science* (Harley, R. M. and Reynolds, T., eds), p. 335. The Royal Botanic Gardens, Kew, Richmond, Surrey, U.K.
5. Sánchez, C., Cárdenas, J., Rodríguez-Hahn, L. and Ramamoorthy, T. P. (1988) *Phytochemistry* **28**, 1681.
6. Ramamoorthy, T. P. (1984) *J. Arnold Arboretum* **65**, 135.
7. Sánchez, C. M. S. (1987) Thesis, Facultad de Química, UNAM.

8. Romanova, A. C., Pribilova, G. F., Sajarov, P. I., Sheichenko, U. J. and Bankovski, A. I. (1971) *Khim. Prirod. Soedinenni* **7**, 199.
9. Nishida, T., Wahlberg, I. and Enzell, C. R. (1977) *Org. Magn. Res.* **9**, 203.
10. Hernández, M., Esquivel, B., Cárdenas, J., Rodríguez-Hahn, L. and Ramamoorthy, T. P. (1987) *Phytochemistry* **26**, 3297.
11. Günther, H. (1980) in *NMR Spectroscopy*, p. 116. John Wiley.