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A DIRHAMNOPYRANOSIDE FROM *PSACALIUM MEGAPHYLLUM**

ANA-L. PÉREZ-CASTORENA, AGUSTÍN CASTRO and ALFONSO ROMO DE VIVAR†

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

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Key Word Index—*Psacalium megaphyllum*; Compositae; sterol glucosides; kaempferol-3-*O*-α-L-(3-*O*-acetyl)rhamnopyranoside-7-*O*-α-L-rhamnopyranoside.

Abstract—A chemical study of *Psacalium megaphyllum* afforded some known compounds and the new, kaempferol-3-*O*-α-L-(3-*O*-acetyl)rhamnopyranoside-7-*O*-α-L-rhamnopyranoside. The structure of the flavonol was determined by spectroscopic methods. © 1997 Elsevier Science Ltd

INTRODUCTION

The American genus *Psacalium* is placed in the 'cacalioid' group of the tribe Senecioneae [1, 2]. Previous studies of the genus showed the presence of furanoeremophilanes [3, 4]. As continuation of our phytochemical research of Mexican plants belonging to this tribe [5–7], we examined *P. megaphyllum*.

RESULTS AND DISCUSSION

Aerial parts of *P. megaphyllum* afforded the new flavonol glycoside **1a** and the known compounds, β-sitosterol, stigmasterol and their glucosides. The last four compounds were identified by comparison with authentic samples.

Compound **1a** $[\alpha]_D -133.6°$, had a molecular formula $C_{29}H_{32}O_{15}$ (high resolution mass spectrum). Its ^1H and ^{13}C NMR spectra (Tables 1 and 2) show the characteristic signals of kaempferol, two rhamnosyl residues and an acetyl group. The signals of the anomeric hydrogens in ^1H NMR spectrum appear as doublets at δ 5.47 and 5.56. These chemical shifts indicate that the monosaccharides are attached to different positions of kaempferol and not as rhamnosyl–rhamnosyl [8]. A comparison of the signals of both sugars shows a downfield shift of H-3″ (Δδ +1.16). The C-3″ signal in the ^{13}C NMR spectrum also presents a downfield shift (Δδ +3.22), and the neighbouring C-atoms exhibit an upfield shift (Δδ −2.01, C-2″ and Δδ −3.22, C-4″). The above-mentioned indicates that the acetyl group is attached to C-3″ of a rhamnopyranose and agrees with the published data for kaempferol-3-*O*-(3-*O*-acetyl-α-L-rhamnopyranoside) [9]. The ^1H NMR spectrum of **1a** in DMSO-d_6–$CDCl_3$–C_6D_6, shows two signals (δ 12.5 and 9.7) that interchange with D_2O. The first is typical for the 5-OH of a 4-ketoflavonoid. The second is assigned to the 4′-OH, since in a NOESY experiment it showed

Table 1. ^1H NMR spectral data of compounds **1a** and **1b**

H	**1a***			**1b**†		
6	6.47	*d*	(1.9)	6.78	*d*	(2.4)
8	6.74	*d*	(1.9)	7.09	*d*	(2.4)
2′,6′	7.83	*d*	(8.9)	7.91	*d*	(8.7)
3′,5′	6.95	*d*	(8.9)	7.28	*d*	(8.7)
1″	5.47	*d*	(1.8)	5.53	*d*	(1.7)
2″	4.37	*dd*	(3.2, 1.8)	5.64	*dd*	(3.3, 1.7)
3″	4.99	*dd*	(9.3, 3.2)	5.26	*dd*	(10, 3.3)
4″	3.55	*t*	(9.3)	4.92	*t*	(10)
5″	3.46	*m*		3.19	*dq*	(10, 6.3)
6″	0.97	*d*	(6.1)	0.87	*d*	(6.3)
1‴	5.56	*d*	(1.8)	5.55	*br s*	
2‴	4.02	*dd*	(3.3, 1.8)	5.43	*bs s*	
3‴	3.83	*dd*	(9.3, 3.3)	5.45	*dd*	(10, 3.5)
4‴	3.48	*t*	(9.3)	5.17	*t*	(10)
5‴	3.62	*m*		3.92	*dq*	(10, 6.2)
6‴	1.26	*d*	(5.9)	1.23	*d*	(6.2)
Ac	2.14	*s*		1.98	*s*	
				2.03	*s*	
				2.06	*s*	
				2.11	*s*	
				2.19	*s*	
				2.32	*s*	
				2.44	*s*	

Assignments based on COSY, HETCOR and LRHETCOR experiments;
* Run at 300 MHz in MeOH-d_4
† Run at 200 MHz in $CDCl_3$.

*Contribution No. 1588 of the Instituto de Química, UNAM.

† Author to whom correspondence should be addressed.

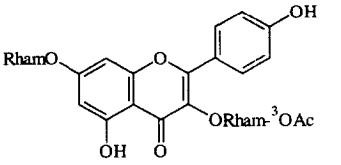
Table 2. ^{13}C NMR spectral data of compounds **1a** and **1b**

C	1a*	1b†
2	159.7	157.5
3	136.2	136.9
4	179.7	180.0
5	162.9	152.7
6	100.6	109.4
7	163.5	168.6
8	95.6	95.8
9	158.1	159.2
10	107.5	112.8
1′	122.3	127.6
2′,6′	131.9	130.1
3′,5′	116.7	122.1
4′	161.8	150.9
1″	102.9	101.8
2″	69.7	69.1
3″	75.3	68.8
4″	70.3	70.5
5″	72.2	68.4
6″	17.7	17.4
1‴	99.8	98.2
2‴	71.7	69.1
3‴	72.1	68.5
4‴	73.6	70.4
5‴	71.3	67.9
6‴	18.1	16.9
Ac	172.8	172.2
	21.1	169.9
		169.6
		21.1
		20.7

Assignments based on DEPT, HETCOR and LRHETCOR experiments.

* Run at 75 MHz in MeOH-d_4.

† Run at 50 MHz in $CDCl_3$.



1a
1b peracetate

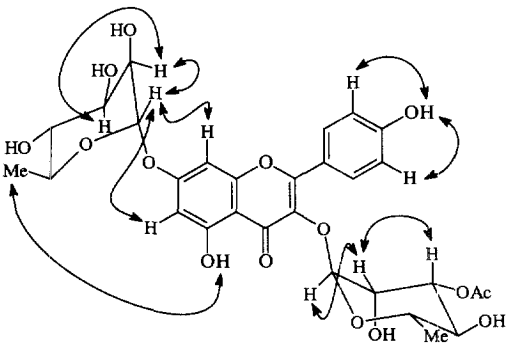


Fig. 1. NOESY correlations of compound **1a**.

correlation with a doublet at δ 6.95 attributed to H-3′ and H-5′ (Fig. 1). That the rhamnopyranose without an acetyl group is joined to the 7-OH was inferred from a NOESY experiment, which showed correlation of the anomeric hydrogen signal with those of H-6 and H-8. A LRHETCOR experiment corroborated the above assumption, since it showed coupling between the H-1‴ and C-7 signals. The 3-*O*-acetylrhamnopyranoside should be attached to the 3-OH in congruity with the downfield shift of the C-2 signal (δ 159.7) compared with those of free kaempferol (δ 146.8) [10, 11]. It also agreed with the long-range coupling between the anomeric hydrogen (H-1″) and C-3, which is shown in the LRHETCOR spectrum. Therefore, the structure of the new flavonol is depicted as **1a** and corresponds to kaempferol-3-*O*-α-L-(3-*O*-acetyl)rhamnopyranoside-7-*O*-α-L-rhamnopyranoside.

The ^1H NMR spectrum of **1a** always showed additional minor signals (δ 5.56, *d*, J = 1.8 Hz, 1H; 5.41, *d*, J = 1.6 Hz, 1H; 5.44, *dd*, J = 3.3, 1.8 Hz, 1H; 3.88, *dd*, J = 9.3, 3.3 Hz, 1H; 0.78, *d*, J = 6.2 Hz, 3H). These are assigned to H-1‴, H-1″, H-2″, H-3″ and H-6″ of the isomer, kaempferol-3-*O*-α-L-(2-*O*-acetyl) rhamnopyranoside-7-*O*-α-L-rhamnopyranoside. The formation of only one peracetylated product (**1b**) on acetylation of the mixture is consistent with the presence of the isomers. The coexistence and easy rearrangement of 2-*O*-acetyl to 3-*O*-acetyl rhamnopyranoside has already been observed in the phytochemical study of *Zingiber zerumbet* [9]. An explanation should be the presence of a chemical equilibrium which is displaced from the axial 2-*O*-acetyl to the equatorial 3-*O*-acetyl derivative.

EXPERIMENTAL

Plant material. Psacalium megaphyllum (Rob. and Greenm.) was collected at the border between Uruapan and Pátzcuaro, Michoacán, in November 1988. A voucher is deposited at the National Herbarium (MEXU 472878).

Extraction and isolation. Dried and ground aerial parts (656 g) were extracted with hexane and Me_2CO. The hexane extract (11.54 g) was purified by CC (Kieselgel G, 173 g) and eluted with a gradient of hexane–EtOAc yielding 24.5 mg of β-sitosterol and stigmasterol as a mixt. The Me_2CO extract (21.15 g) was purified by CC (Kieselgel G, 318 g) and eluted with mixt. of hexane–EtOAc. The frs eluted with hexane–EtOAc (3:7) gave a mixt. of β-sitosterol and stigmasterol glucosides (60 mg). The substances were identified by comparison with authentic samples and by acetylation and hydrolysis products. The frs eluted with hexane–EtOAc (1:9) were purified by two successive CCs. The first was eluted with hexane–EtOAc (3:7), the second with $CHCl_3$–Me_2CO (3:7), to give 326 mg of **1a**.

Compound **1a**. Yellow powder, mp 188–189° from

$CHCl_3$–Me_2CO. $[\alpha]_D$ −133.6° (*c* 0.22, MeOH). UV λ_{max}^{MeOH} nm (log ε): 265 (4.24), 342 (4.08). IR ν_{max}^{KBr} cm^{-1}: 3421, 1739, 1660, 1601. FAB-MS (nitrobenzyl alcohol) *m/z*: 621 $[M+1]^+$, 433 $[621\text{-}C_8H_{12}O_5]^+$, 287 $[433\text{-}C_6H_{10}O_4]^+$, 189 $[C_8H_{13}O_5]^+$, 136 $[A+1\text{-}C_6H_{10}O_5]^+$, 107 $[A\text{-}C_6H_{10}O_5\text{-}CO]^+$, 43 $[C_2H_3O]^+$. EIMS 70 eV *m/z* (rel. int.): 286 $[M\text{-}C_8H_{12}O_5\text{-}C_6H_{10}O_4]^+$ (100), 189 (10), 147 $[C_6H_{11}O_4]^+$ (6.4), 129 [189-AcOH]$^+$ (13), 111 [129-$H_2O]^+$ (18), 43 $[C_2H_3O]^+$ (84.1). observed 621.1816 $[M+1]^+$, calcd for $C_{29}H_{33}O_{15}$ 621.1819.

Compound **1b**. **1a** (34.8 mg) acetylated in the usual manner afforded 20.3 mg of **1b** mp 116–118° from hexane–Me_2CO. IR ν_{max}^{nujol} cm^{-1}: 1751, 1633, 1616. FAB-MS (nitrobenzyl alcohol) *m/z*: 957 $[M+1]^+$, 915 $[957\text{-}C_2H_2O]^+$, 642 $[915\text{-}C_{12}H_{17}O_7]^+$, 273 $[C_{12}H_{17}O_7]^+$, 153 [273-2AcOH]$^+$, 111 $[153\text{-}C_2H_2O]^+$, 43 $[C_2H_3O]^+$.

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