The Final Structures of the Lichen Chromones Galapagin, Lobodirin, Mollin, and Roccellin

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Lichens, Chromone Glucosides, NOE Difference Spectra

The structures of the lichen chromones galapagin, lobodirin, mollin, and roccellin, specific compounds of Roccellaceae (lichens), have been established as **1, 2, 3,** and **4,** respectively, by NOE difference spectroscopy.

In 1972 and 1973, Huneck described the isolation of roccellin, mollin, galapagin [1], and lobodirin [2], hitherto known only from certain taxa of Roccellaceae (Ascolichenes), and recognized these compounds as partially acetylated chromone glucosides. The position of the acetyl groups could not be determined at that time. Now we have elucidated the full structures of these lichen chromones by application of NOE difference spectroscopy and report here on our results.

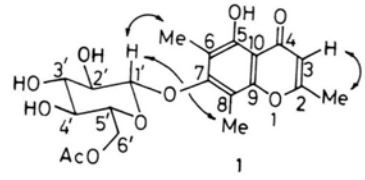
Galapagin is 8-methyleugenitol-7-O-β-D-6′-O-acetyl-glucopyranoside (**1**), because the ^{1}H NMR spectrum shows three doublets at δ 5.68, 5.21, and 5.26 ppm, corresponding to the hydroxyl groups at C-2′, C-3′, and C-4′ (Table I).

Lobodirin is isoeugenitol-7-O-β-D-2′,3′,6′-tri-O-acetyl-glucopyranoside (**2**), because there is the doublet of the free 4′-OH-group which is coupled with the 4′-proton.

Mollin is a derivative of eugenitol and shows no 2′-OH signal in its ^{1}H NMR spectrum (in DMSO-d_6). Because there is only one signal of an acetyl-Me group, the acetoxy group must be situated at C-2′, which means that mollin is eugenitol-7-O-β-D-2′-O-acetyl-glucopyranoside (**3**).

The ^{1}H NMR spektrum of roccellin reveals 2 singulets of 2 acetyl-Me groups at 1.90 and 2.08 ppm (in DMSO-d_6) and 2.11 and 2.17 ppm (in $CDCl_3$), respectively, but no signals of the 2′- and 6′-OH groups; hence roccellin is eugenitol-7-O-β-D-2′,6′-di-O-acetyl-glucopyranoside (**4**). The methyl signals in the ^{1}H NMR spectrum of acetyl-roccellin (**5**) could be correlated by their chemical shifts and NOE difference spectra. The methyl group corresponding to the singulet at 2.30 ppm gives a NOE with the proton at C-3 and hence is the methyl group at C-2. NOE's are also observed between the acetyl-Me group at C-5 (s 2.45 ppm) and the Me-group at C-6 (s 2.02 ppm).

^{13}C NMR data of galapagin, mollin, and acetyl-roccellin are given in Table II.



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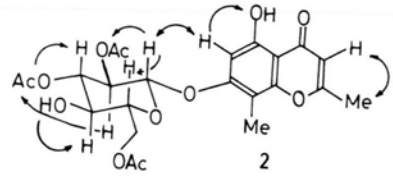

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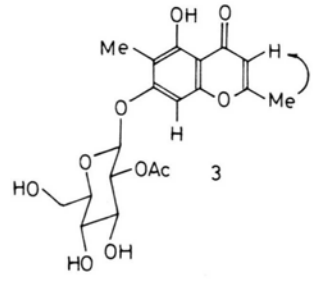

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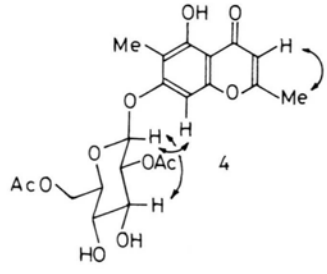

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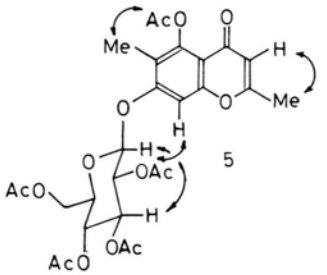
Table I. ^{1}H NMR chemical shifts and coupling constants of galapagin (**1**), lobodirin (**2**), mollin (**3**), roccellin (**4**), and acetylroccellin (**5**).

	1 400 MHz DMSO-d_6	**1** 400 MHz acetone-d_6	**2** 400 MHz $CDCl_3$	**3** 250 MHz DMSO-d_6	**4** 400 MHz DMSO-d_6	**4** 400 MHz $CDCl_3$	**5** 400 MHz $CDCl_3$
H-3	s 6.27	q 6.16	s 6.05	s 6.27	s 6.26	s 6.06	s 5.99
H-6	–	–	s 6.48	–	–	–	–
H-8	–	–	–	s 6.76	s 6.74	s 6.56	s 6.89
H-1′	d 4.64	d 4.79	d 5.09	d 5.32	d 5.30	d 5.03	d 5.12
H-2′	m 3.34	m 3.57	dd 5.31	dd 4.87	dd 4.88	dd 5.18	dd 5.38
H-3′	ddd 3.25	m 3.50	dd 5.14	m 3.53	ddd 3.55	ddd 3.76	dd 5.33
H-4′	ddd 3.18	m 3.42	ddd 3.67	ddd 3.28	ddd 3.30	ddd 3.58	dd 5.17
H-5′	m 3.30	m 3.42	ddd 3.74	m 3.50	ddd 3.84	ddd 3.71	dt 3.98
H-6′$_1$	m 4.11	m 4.24	dd 4.38	m 3.50	dd 4.08	dd 4.40	d 4.26
H-6′$_2$			dd 4.54	dd 3.75	dd 4.38	dd 4.55	
C-2-Me	s 2.42	d 2.45	s 2.39	s 2.39	s 2.38	s 2.35	s 2.30
C-6-Me	s 2.13	s 2.19	–	s 2.03	s 2.11	s 2.05	s 2.02
C-8-Me	s 2.16	s 2.31	s 2.16	–	–	–	–
5-OH	s 12.92	s 12.97	s 12.67	s 13.05	s 13.01	s 12.85	–
2′-OH	d 5.68	d 4.84	–	–	–	–	–
3′-OH	d 5.21	d 4.43	–	d 5.45	d 5.56	d 2.78	–
4′-OH	d 5.26	d 4.49	d 3.07	d 5.35	d 5.61	d 3.09	–
6′-OH	–	–	–	dd 4.73	–	–	–
2′-OAc	–	–	s 2.07	s 1.89	s 2.08	s 2.17	s 2.08
3′-OAc	–	–	s 2.09	–	–	–	s 2.07
4′-OAc	–	–	–	–	–	–	s 2.06
6′-OAc	s 1.89	s 1.89	s 2.14	–	s 1.90	s 2.11	s 2.13

J (Hz): 1′,2′ = 7.5; 2′,3′ = 3′,4′ = 4′,5′ ~ 9.5; 5′,6_1′ = 2.5; 5′,6_2′ = 5; 6_1′,6_2′ = 12; 2′,OH = 3′,OH = 6′,OH ~ 5.

Table II. ^{13}C NMR chemical shifts of galapagin (**1**), mollin (**3**), and acetylroccellin (**5**). Shifts marked [a] and [b] may be interchangeable.

C Atom	Compound **1** (67.9 MHz, DMSO-d_6)	**3** (62.76 MHz, DMSO-d_6)	**5** (67.9 MHz, DMSO-d_6)
2 (C)	168.44	168.39	169.10
3 (CH)	108.04	108.37	111.61
4 (CO)	182.67	182.27	176.25
5 (C)	152.56[a]	158.13	156.52
6 (C)	109.70	108.51	119.00
7 (C)	158.51[a]	155.55	147.81
8 (C,CH)	114.31	97.72[b]	100.50
9 (C)	155.93	160.28	158.48
10 (C)	106.54	105.00	112.15
11 (CH_3)	8.84	6.92	8.49
12 (CH_3)	8.89	–	–
13 (CH_3)	20.04	19.88	20.00
1′ (CH)	104.26	93.10[b]	98.59
2′ (CH)	76.04	77.34	72.40
3′ (CH)	73.91	74.54	72.38
4′ (CH)	69.97	69.74	68.26
5′ (CH)	73.36	73.31	70.69
6′ (CH_2)	63.05	60.51	61.96
2′-OCO−$\underline{C}H_3$	–	20.69	10.57 (4×)
6′-OCO−$\underline{C}H_3$	20.37	–	
3′-OCO−$\underline{C}H_3$	–	–	10.98
4′-OCO−$\underline{C}H_3$	–	–	
2′-O$\underline{C}$O−CH_3	–	169.59	170.40 (2×)
6′-O$\underline{C}$O−CH_3	170.06	–	
3′-O$\underline{C}$O−CH_3	–	–	170.41
4′-OCO−CH_3	–	–	169.38 (2×)



NOE's in the formulae 1–5 are marked by arrows.

Experimental

The NMR spectra were recorded on Bruker AM 400, AM 270, and 250 MHz instruments.

Galapagin (**1**)

MS, *m/z* 466.1475 (M^+; calcd for $C_{22}H_{26}O_{11}$: 466.1475), 424.13693 ($M-CH_2=C=O$; calcd for $C_{20}H_{24}O_{10}$: 424.13693), 220.0733 ([8-methyleugenitol]$^{+\cdot}$; calcd for $C_{12}H_{12}O_4$: 220.0735).

Roccellin (**4**)

MS, *m/z* 206.0577 ([eugenitol]$^{+\cdot}$; calcd for $C_{11}H_{10}O_4$: 206.0579).

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[1] S. Huneck, J. Prakt. Chem. **314,** 488 (1972).

[2] S. Huneck, Phytochemistry **12,** 2497 (1973).