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ANTHRAQUINONES IN *CALOPLACA**

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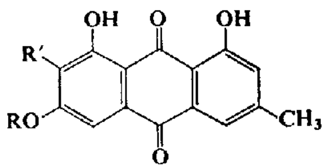
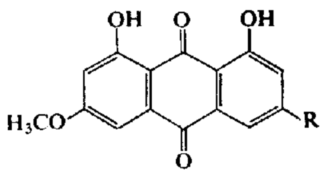
Abstract—About 230 species of the lichen genus *Caloplaca* have been surveyed for anthraquinones. By means of lichen mass spectrometry and TLC, emodin, parietin, fallacinol, fallacinal, parietinic acid, xanthorin, 2-chloroemodin, fragilin, and 1-*O*-methylfragilin have been identified, as well as some non-anthraquinonoid compounds. The species studied can be arranged according to their anthraquinone content in thirteen "chemical groups".

INTRODUCTION

Caloplaca is one of the larger lichen genera and the largest within the family Teloschistaceae. The exact number of *Caloplaca* species is unknown, since the genus has not been monographed, but it is probably in the order of 500. The species are crustose and sometimes also lobate (sect. *Gasparrinia*). The apothecia are usually yellow to dark brown red, the thallus in many cases possessing a similar but usually lighter colour.



	R	R′
(I)	CH_3	H
(II)	H	H
(III)	CH_3	Cl
(IV)	H	Cl



(V) R = CH_2OH
(X) R = CHO
(XI) R = COOH

The colour has generally been believed to be due to the presence of parietin (I), although "identifications" of I have usually only been based on the deep-red coloration obtained upon application of aqueous KOH ("K+ red", "K+ violet", etc.).

Rather few chemical studies have been made. Zopf isolated parietin from *C. cirrochroa*,[1] *C. aurantia*,[2] *C. flavovirescens*,[1] and *C. jungermanniae*,[3] while Hesse found it in *C. murorum* and *C. decipiens*.[4] Hesse also studied *C. arenaria*[5] and *C. percrocata*;[6] these species were

* Part XXIX in the series "Chemical Studies on Lichens"; for Part XXVIII see: J. SANTESSON, *Acta Chem. Scand.* **24**, 371 (1970).

[1] W. ZOPF, *Ann.* **297**, 271 (1897).
[2] W. ZOPF, *Ann.* **321**, 37 (1902).
[3] W. ZOPF, *Ann.* **346**, 82 (1906).
[4] O. HESSE, *J. Prakt. Chem.* **58**, 409 (1898).
[5] O. HESSE, *J. Prakt. Chem.* **58**, 465 (1898).
[6] O. HESSE, *J. Prakt. Chem.* **63**, 522 (1901).

recently re-investigated by Bohman,[7] who found parietin (I), emodin (II), fragilin (III), and 2-chloroemodin (IV).[8] Bohman also studied *C. ferruginea, C. verruculifera, C. obliterans,* and *C. aurantiaca.*[7] Other investigations have been made on *C. cinnabarina,*[9] *C. aurantia*[10] and *C. regalis.*[11]

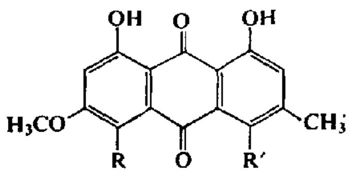
The aim of the present investigation has been to study the pigments of some 230 *Caloplaca* species. It is a part of a phytochemical study of the family Teloschistaceae.[12] Independent of the present work, Steiner *et al.* have studied the anthraquinones of about fifty *Caloplaca* species.[13]

RESULTS AND DISCUSSION

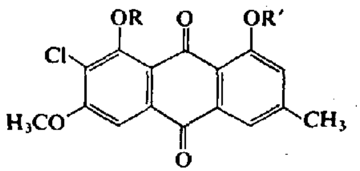
Methods

Since often only the apothecia are pigmented, these have as far as possible been investigated; apothecia were also studied in those species with a coloured thallus, in order to obtain comparable results. No special precautions have been taken to ensure that the investigated apothecia were completely free from adhering thallus fragments.

The small size of the apothecia (sometimes less than 0·4 mm dia.) has necessitated the use of the "lichen mass spectrometry" (LMS) method.[14] With this method it is not possible to differentiate between fallacinol (V), xanthorin (VI), and erythroglaucin (VII), all having $M^{+\cdot} = m/e$ 300. Furthermore, only information on the relative amounts of pigment



	R	R′
(VI)	OH	H
(VII)	H	OH



	R	R′
(VIII)	CH_3	H
(IX)	H	CH_3

present can be obtained (the most abundant compound taken as 100%). These semiquantitative data are however believed to be accurate within a factor of $10^{\pm 0 \cdot 5}$ and in Table 1 they are given using a logarithmic scale[15] with each step corresponding to the factor $10^{0 \cdot 5}$. The

[7] (a) G. BOHMAN, *Phytochem.* **8**, 1829 (1969); (b) G. BOHMAN, *Phytochem.* **9**, 461 (1970).
[8] The numbering is based on emodin, 1,3,8-trihydroxy-6-methylanthraquinone.
[9] S. H. HARPER and R. M. LETCHER, *Proc. Trans. Rhodesian Sci. Assoc.* **51**, 156 (1966).
[10] G. HAUSCHILD, M. STEINER and K. W. GLOMBITZA, *Naturwiss.* **55**, 346 (1968).
[11] S. HUNECK and G. FOLLMANN, *Z. Naturforsch.* **21b**, 91 (1966).
[12] Some preliminary results were presented at "Botaniker-Tagung der Deutschen botanischen Gesellschaft" in Berlin, 6 October 1969.
[13] M. STEINER, *Ber. Deut. Bot. Ges., Vortr. Gesamtg. Bot., N.F.* **4**, 23 (1970).
[14] J. SANTESSON, *Arkiv Kemi* **30**, 363 (1969).
[15] The reason for the use of a logarithmic scale in the determination of compounds by LMS is as follows. The constant error is very small compared with the error introduced by the uneven evaporation in the mass spectrometer inlet system of the compounds present. This latter error is directly dependant upon the amounts present of a compound. As the relative amount of a compound decreases, this error, expressed in per cent of the relative amount present of the compound, will remain about the same, but, when expressed in per cent of the most abundant compound, it will decrease. Hence at lower concentrations more precise distinctions—with regard to the most abundant compound—can be made.

TABLE 1. ANTHRAQUINONES IN *Caloplaca* SPECIES

No.	Group	Species	Anthraquinones: Em.	Pa.	Fo., X., Er.	Fa.	Pa-a.	Cl-Em.	Fr.	Other compounds
1	A	*abbreviata* Malme	4	6	3	3				
2	A	*acheila* Zahlbr. f. *rubentior* Zahlbr.	3	6	4	3				
3	L	*agardhiana* (Flot.) Flag.								
4	A	*albidella* (Tuck.) Zahlbr.		6						At., 402
5	L	*albovariegata* B. de Lesd.‡								
6	A	*allanii* Zahlbr.	3	6	3	3				
7	A	*altoandina* (Malme) Zahlbr.	4	6	4	6				
8	A	*americana* (Malme) Zahlbr.	4	6	4*	4				
9	A	*americana* (Malme) Zahlbr.	3	6	4	4				
10	F-2	*ammiospila* (Wahlenb. in Ach.) Oliv.	6	6				6	5	
11	A	*applanata* H. Magn.	3	6	3	3	1			
12	A	*approximata* (Lynge) H. Magn.	3	6	2	3				
13	A	*aractina* (Fr.) Häyrén	4	6	3	3				
14	A	*aractina* (Fr.) Häyrén	4	6	5	3				
15	A	*arctica* H. Magn.	4	6	3	3	3			
16	F-2	*areolata* (Zahlbr.) Clauz.	5	5				5	6	
17	A	*argillacea* (Malme) Zahlbr.	5	6	3	3	3			
18	J	*arizonica* H. Magn.	6	6					5	
19	A	*arnoldiana* (Serv. et Cern.) Serv. et Poelt in Poelt	4	6	4	3				
20	A	*arnoldii* (Wedd.) Zahlbr.	3	6	3	2				
21, 22	L	*assigena* (Lahm) Arn.								
23, 24	L	*atrocyanescens* (Th. Fr.) Oliv.								
25	L	*atrocyanescens* f. *subochracea* H. Magn.								
26	A	*atroflava* (Turn.) Mong.	3	6	3	4				
27	A	*aurantia* (Pers.) Hellb. v. *aurantia*	3	6	3	1				
28	G	*aurantiaca* (Lightf.) Th. Fr.§	4	6	2	3			4	
29	G	*aurantiaca* (Lightf.) Th. Fr.	5	6	3	3			4	
30, 31	G	*aurantiaca* (Lightf.) Th. Fr.	4	6	3	3			4	
32	G	*aurantiaca* (Lightf.) Th. Fr.	5	6	3	4			5	
33	G	*aurantiaca* (Lightf.) Th. Fr.	5	6	3	3			5	
34	G	*aurantiaca* (Lightf.) Th. Fr.	4	6	3	4			4	
35	G	*aurea* (Schaer.) Zahlbr.	4	6		3			4	02
36	G	*aurea* (Schaer.) Zahlbr.	4	6	2	3			4	02
37	A	*biatorina* (Mass.) Stein.	3	6	3	3				
38	A	*biatorina* v. *baumgartnerii* (Zahlbr.) Poelt	3	6	4	2				
39	A	*bolacina* (Tuck.) Herre	3	6	3	3				

TABLE 1—*cont.*

No.	Group	Species	Anthraquinones							Other compounds
			Em.	Pa.	Fo., X., Er.	Fa.	Pa-a.	Cl-Em.	Fr.	
40	A	*bolanderi* (Tuck.) H. Magn.	3	6	3	1				
41	A	*brachyloba* (Müll. Arg.) Zahlbr.	4	6	3*	4				402
42	A	*brachyspora* Meresch.	3	6	2	2				
43	E	*brebissonii* (Fée)	5					6		*Li.*
44	A	*britannica* R. Sant. (ined.)	3	6	3*	2	2			
45	A	*brouardi* (B. de Lesd.) Zahlbr.	4	6	3	4				
46	F-1	*byrsonimae* (Malme) Zahlbr.	4	6	3	4		3	6	
47	A	*cacuminum* Poelt	3	6	2	2				
48	F-1	*caesiorufa* (Wiebel) Flag.	4	6	2	3		5	4	
49	F-1	*caesiorufa* (Wiebel) Flag.	4	6	3	3		5	4	
50	A	*caesiorufella* (Nyl.) Zahlbr.	4	6	3	3				
51	A	*californica* Zahlbr.	3	6	2	2				
52	L	*camptidia* (Tuck.) Zahlbr.								
53	L	*capitulata* H. Magn.								
54	A	*carolinae* H. Magn.	4	6	4*	4				
55	B	*carphinea* (Fr.) Jatta	4	6						*Us.*
56	B	*carphinea* (Fr.) Jatta	3	6						*Us.*
57	A	*cerina* (Ehrh.) Th. Fr.	3	6	3	3				
58	A	*cerinella* (Nyl.) Flag.	4	6	4	3				
59	A	*cerinoides* (Anzi) Jatta	3	6	4	4				
60	L	*chalybaea* (Fr.) Müll. Arg.								
61	A	*chapadensis* (Malme) Zahblr.	3	6	4	3				
62	A	*chlorina* (Flot.) Sandst.	4	6	3	3	3			
63	G	*chrysophthalma* Degel.	5	6					5	
64	A	*cinnabarina* (Ach.) Zahlbr.	4	6	4	3	3			
65	A	*cinnabarina* v. *subrubelliana* (Vain.) Zahlbr.	3	6	4	4				
66	F-1	*cinnamomea* (Th. Fr.) Oliv.	4	6	2	3		4	3	
67	F-1	*cinnamomea* (Th. Fr.) Oliv.	4	6	3	3		5	4	
68	F-1	*cinnamomea* (Th. Fr.) Oliv.	6	6	4*	4		6	4	
69	A	*cirrochroa* (Ach.) Th. Fr.	3	6	3	3				
70	A	*citrina* (Hoffm.) Th. Fr.	3	6	2	2				
71	A	*citrina* (Hoffm.) Th. Fr.	3	6	3	3				
72	A	*citrina* (Hoffm.) Th. Fr.‖	4	6	3	3	3			
73	A	*cladodes* (Tuck.) Zahlbr.	3	6	3	2				
74	A	*commixta* (Malme) Zahlbr.	4	6	5*	4	5			
75	F-2	*concilians* (Nyl.) Oliv.	5	6				6	3	

76	A	*conglomerata* (Bagl.) Jatta	5	6	4	3				
77	A	*congrediens* (Nyl.) Zahlbr.	4	6	3	3				
78	A	*congrediens* (Nyl.) Zahlbr.	5	6	3	3	1			
79	L	*conversa* (Krempelh.) Jatta								
80	A	*coracina* (Vain.) Poelt	4	6	2	2				
81	A	*coralloides* (Tuck.) Hult.	3	6	4	2				
82	A	*coronata* (Krempelh.) Steiner	4	6	4	2				
83	A	*crocina* (Krempelh.)	6	6	3	3				
84	A	*crosbyi* Zahlbr. in H. Magn.	3	6	3	1				
85	B	*cuyabensis* (Malme) Zahlbr.	5	6		4				Us.
86	A	*dalmatica* (Mass.) Zahlbr.	3	6	3	3				
87	A	*decipiens* (Arn.) Blomb. et Forss.	4	6	4	3				
88	H	*declarata* (Nyl.) Oliv.	6	4				6		
89	L	*diducenda* (Vain.) Zahlbr.								
90	L	*diphyodes* (Nyl.) Jatta								
91	L	*diplacia* (Ach.) Riddle								402
92	L	*diplacia* v. *carneofusca* (Nyl. ex Cromb.) Zahlbr.								402
93	A	*discernenda* (Nyl.) Zahlbr.	3	6	3	3				
94	H	*discoidalis* (Vain.) Lynge	4	3				6		
95	F-2	*discolor* (Willey) Fink	5	5				6	6	
96	F-2	*discolor* (Willey) Fink	4	5				6	6	
97	A	*dolomiticola* (Hue) Zahlbr.	3	6	3	3				
98	A	*dolomiticola* (Hue) Zahlbr.	3	6	2	3				
99	A	*dovrensis* H. Magn.¶	3	6	2	3				
100	F-1	*epithallina* Lynge	5	6	3	3		6	4	
101	E	*erythrantha* (Tuck.) Zahlbr.	5					6		
102	E	*erythrantha* (Tuck.) Zahlbr.**	5					6		
103, 104	E	*erythrantha* (Tuck.) Zahlbr.	5					6		
105	F-2	*erythranthoides* (Vain.) Zahlbr.	4	3				5	6	
106	F-2	*erythranthoides* (Vain.) Zahlbr.	4	3				6	6	
107	F-2	*erythranthoides* (Vain.) Zahlbr.	6	4				6	6	
108	I	*erythrocarpa* (Pers.) Zw.	4					6	5	
109	I	*erythrocarpa* (Pers.) Zw.	5					6	6	
110	I	*erythrocarpa* (Pers.) Zw.	5					6	6	
111	A	*exsecuta* (Nyl.) DT. et Sarnth.	4	6	4	4	3			
112	A	*fallax* (Bagl.) Jatta	4	6	3	3				
113	A	*feracissima* H. Magn.	3	6	2	3				
114	A	*ferrarii* (Bagl.) Jatta	4	6	3	3				
115	F-1	*ferruginea* (Huds.) Th. Fr.	5	6	3	3		5	4	
116	F-1	*erruginea* (Huds.) Th. Fr.	5	6	3	3		5	5	
117	F-2	*festiva* (Ach.) Zw.	5	5				6	5	
118	F-2	*festiva* (Ach.) Zw.	5	4				6	6	
119	F-2	*festiva* (Ach.) Zw.	5	6				5	4	

TABLE 1—*cont.*

No.	Group	Species	Anthraquinones: Em.	Pa.	Fo., X., Er.	Fa.	Pa-a.	Cl-Em.	Fr.	Other compounds
120	F-2	*festiva* (Ach.) Zw.	5	4				6	4	
121	A	*festivella* (Nyl.) Kieffer	5	6						
122	G	*flavovirescens* (Wulf.) DT. et Sarnth.	6	6		4			6	332
123	G	*flavovirescens* (Wulf.) DT. et Sarnth.	5	6		4			6	332
124	G	*flavovirescens* (Wulf.) DT. et Sarnth.	4	5		3			6	332
125	G	*flavovirescens* (Wulf.) DT. et Sarnth.	5	6		3			6	332
126	G	*flavovirescens* (Wulf.) DT. et Sarnth.	5	6	3	4			6	332
127, 128	L	*floridana* (Tuck.)								
129	A	*fraudans* (Th. Fr.) Oliv.	4	6	3	4				
130	A	*fraudans* (Th. Fr.) Oliv.	4	6	3	3				
131	A	*friesii* H. Magn.	4	6						
132	F-2	*furfuracea* H. Magn.	6	6				6	4	
133	F-1	*fuscorufa* H. Magn.	5	6	3	4		5	3	
134	A	*germanica* H. Magn.	4	6	3	4	3			
135	F-2	*granularis* (Müll. Arg.) Zahlbr.	4	6				3	6	
136	A	*granulifera* (Müll. Arg.) Jatta	4	6	4*	5				402
137	A	*granulosa* (Müll. Arg.) Jatta	3	6	3	2				
138	A	*haematites* (Chaub. ex Saint-Amans) Zw.	3	6	3	3				
139	C	*haematodes* (Mass.) Zahlbr.	4	6	6†	4				
140	C	*haematodes* (Mass.) Zahlbr.	5	5	6*,†					
141	A	*heppiana* (Müll. Arg.) Zahlbr.	3	6	3	3				
142	A	*herbidella* (Nyl.) H. Magn.	5	6	3	4				
143	A	*herminiaca* Samp.	5	6	3	4				
144	G	*hokkadensis* Räs.	3	5					6	
145	A	*holocarpa* (Hoffm.) Wade	3	6	3	3				
146	A	*holocarpa* (Hoffm.) Wade††	3	6	3	3				
147	A	*holocarpa* (Hoffm.) Wade‡‡	4	6	4*	5				
148	A	*holocarpa* (Hoffm.) Wade‡‡	4	6	6*,†	6	3			
149	A	*holocarpa* (Hoffm.) Wade§§	4	6	3	2				
150	A	*hungarica* H. Magn.	4	6	3	3				
151	A	*inconnexa* (Nyl.) Zahlbr.	4	6	3	5				
152	A	*inconstans* Zahlbr. in H. Magn. et Zahlbr.	3	6	3	3				
153	A	*insularis* Poelt	4	6	3	3				
154	A	*interfulgens* (Nyl.) Steiner	3	6	3	2	2			
155	A	*invadens* Lynge	3	6	2	2				
156	A	*irrubescens* (Nyl.) Zahlbr.	4	6	4*	4				

157	A	*isidioclada* Zahlbr.	5	6	3	3				
158	F-2	*isidiosa* (Vain.) Zahlbr.	3	4					6	402
159	A	*jemtlandica* H. Magn.	4	6		4				
160	A	*jungermanniae* (Vahl) Th. Fr.	4	6	2	3				
161	A	*kamczatica* (Sav.) Zahlbr.	4	6	6*					
162	A	*keissleri* Serv.¶	4	6	3	3				
163	A	*lactea* (Mass.) Zahlbr.	5	6	3	3				
164	A	*laeta* H. Magn.	3	6	2					
165	A	*lamprocheila* (DC.) Flag.	5	6	3	3				
166	A	*latispora* (Lynge) H. Magn.	3	6	3	3				
167	F-1	*leptocheila* H. Magn.	5	6	4*	4		6	6	
168	F-1	*leptocheila* v. *tenuis* H. Magn.	5	6	3	3		4	4	
169	A	*ligustica* B. de Lesd.	5	6	3	4				
170	B	*limitosa* (Nyl.) Oliv.	4	6	3	3				Us.
171	A	*littorea* C. Tav.	3	6	3	2				
172	A	*livida* (Hepp) Jatta	5	6	3	4				
173	A	*lobulata* (Flk.) Hellb.	3	6	4	4				
174	A	*lucens* (Nyl.) Zahlbr.	3	6	4*	4	2			
175	A	*luteoalba* (Turn.) Th. Fr.	3	6	3	2				
176	A	*magni-filii* Poelt	5	6	3	3	2			
177	A	*malmeana* Zahlbr.	4	6	4*	5	2			
178	A	*marina* (Wedd.) Zahlbr.	3	6	3	2				
179	A	*marmorata* (Bagl.) Jatta	6	6	3	4				
180	A	*melanocheila* (Malme) Zahlbr.	4	6	3	3				402
181	A	*mexicana* B. de Lesd.‖‖	4	6	3	3				
182	A	*microphyllina* (Tuck.) Hasse	3	6	4*	4	2			
183	A	*microphyllina* (Tuck.) Hasse	3	6	4	2				
184	A	*microthallina* (Wedd.) Zahlbr.	3	6	2	2				
185	A	*microthallina* (Wedd.) Zahlbr.	3	6	3	2				
186	A	*microthallina* (Wedd.) Zahlbr.¶¶	4	6	3*	2	2			
187	A	*montevidensis* H. Magn.	3	6	3	2				
188	A	*murorum* (Ach.) Th. Fr.	4	6	4*	3				
189	A	*murorum* (Ach.) Th. Fr.		6	5*	3				
190	A	*murorum* (Ach.) Th. Fr.***	4	6	3	3	2			
191	A	*murorum* v. *granuliformis* (Vain.) Zahlbr.	3	6	4	3				
192	A	*mydalaea* (Körb.) Zahlbr.	4	6	3	3				
193	A	*muelleri* (Vain.) Zahlbr.	4	6	4*	5				
194	A	*muelleri* (Vain.) Zahlbr.	3	6	4	4				
195	A	*myriocarpa* (Malme) Zahlbr.	3	6	3	3				
196	A	*necator* Poelt et Clauz.	5	6	6*	6	4			
197	A	*nideri* Steiner	4	6	5*	4	2			
198	A	*nivalis* (Körb.) Th. Fr.	3	6	2	2				
199	A	*nubigena* (Krempelh.) DT. et Sarnth.	3	6	3	3				

TABLE 1—*cont.*

No.	Group	Species	Anthraquinones Em.	Pa.	Fo., X., Er.	Fa.	Pa-a.	Cl-Em.	Fr.	Other compounds
200	A	*obliterans* (Nyl.) Blomb. et Forss.	3	6	3	2				
201	L	*obscurella* (Lahm) Th. Fr.								
202, 203	A	*ochracea* (Schaer.) Flag.	4	6	2	3				
204	J	*orthoclada* Zahlbr.		*4*				*3*	*6*	
205	A	*paepalostoma* (Anzi) Jatta	4	6						
206	L	*pallescens* H. Magn.								*Li.*
207	A	*paulii* Poelt	3	6	3	2				
208	A	*peragrata* (Fée) Steiner	4	6						402
209	A	*peragrata* (Fée) Steiner	4	6	3	4				402
210	A	*percrocata* (Ach.) Steiner	5	6	3	3				
211	A	*pergracilis* Zahlbr.	*4*	*6*	*5**	*5*	*5*			
212	A	*phaeocarpella* (Nyl.) Zahlbr.	4	6	2	2				
213	A	*pollinii* (Mass.) Jatta	*6*	*6*	3	3				
214	A	*polycarpa* (Mass.) Zahlbr.	4	6	4	2				
215	A	*polycarpa* (Mass.) Zahlbr.	3	6	3	3				
216	A	*proteus* Poelt	3	6	4					
217	A	*puiggarii* (Müll. Arg.) Zahlbr.	*4*	*6*	3	*4*				
218	A	*punctiformis* (Vain.) Zahlbr.	3	6	3	3				
219	A	*pusilla* (Mass.) Zahlbr.	3	6	4	3				
220	L	*pyraceoides* B. de Lesd.								
221	A	*regalis* (Vain.) Zahlbr.	3	6	3	2				
222	A	*rinodinoides* Steiner	3	6	3	3				
223	A	*rubelliana* (Ach.) Lojka	3	*6*	*5**	*4*				
224	A	*rubina* Zahlbr.	3	6	3	2				
225	A	*rugulosa* (Nyl.) Zahlbr.	*5*	*6*						
226	L	*russeola* (Nyl.) Zahlbr.								*Li.*
227	L	*sarcopisoides* (Körb.) Zahlbr.								
228	A	*saxifragarum* Poelt	4	6	3	2				
229	L	*sbarbaronis* B. de Lesd.								
230	J	*scabrida* H. Magn.		*4*					*6*	
231	A	*schaereri* (Arn.) Zahlbr.	3	6	3	3				
232	A	*scopularis* (Nyl.) Lettau	3	6	3	2				
233	A	*scopularis* (Nyl.) Lettau	3	6	3	3				
234	A	*scotoplaca* (Nyl.) H. Magn.	*5*	*6*	3	3				
235	A	*scotoplaca* (Nyl.) H. Magn.	5	6	3	3				

236	A	*selkirkii* Zahlbr.	3	6	3	3				
237	F-2	*serenior* (Vain.) Zahlbr.	4	4				5	6	
238	D	*sibirica* H. Magn	6	5						*At.*
239	A	*sideritis* (Tuck.) Zahlbr.	4	6	2	2				
240, 241	D	*sinapisperma* (Lahm) Mah. et Gill.	6	6						*At.*
242, 243	D	*sinapisperma* (Lahm) Mah. et Gill.	6	4						At.
244	I	*spalatensis* Zahlbr.						6	6	
245	A	*spaldingii* Zahlbr.	4	6	4	6	2			
246	F-2	*spitsbergensis* H. Magn.	4	5				6	3	
247	F-2	*spitsbergensis* H. Magn.	5	3				6	3	
248	A	*spotornensis* B. de Lesd.	5	6	3	3				
249	A	*stanfordensis* H. Magn.	3	6	4*	3				
250	B	*stenospora* (Malme) Zahlbr.	5	6	3	3				*Us.*
251	A	*stillicidiorum* (Vahl) Lynge	4	6	3	4	1			
252, 253	E	*subathallina* H. Magn.	4					6		
254	F-2	*subaurantiaca* (Fée) Zahlbr.	5	4				6	6	
255	A	*subcerata* (Stiz.) Zahlbr.	4	6	5	5				
256	A	*suberythrella* (Nyl.) Clauz. et Rond.	3	6	4	4				
257	A	*subfulgescens* (Nyl.) Zahlbr.	4	6	3	2				
258	A	*sublobulata* (Nyl. Zahlbr.)	3	6	1	2				
259	A	*submergenda* (Nyl.) Oliv.	4	6	2	2				
260	A	*subnitida* (Malme) Zahlbr.	3	6	3	3				
261	A	*subnitida* (Malme) Zahlbr.	4	6	3	3				
262	A	*subpallida* H. Magn.	5	6	4*	3	4			
263	A	*subsoluta* (Nyl.) Zahlbr.	4	6	5*	5	3			
264	A	*subunicolor* (Nyl. ex. Cromb.) Zahlbr.		6	2	2				
265	A	*subvitellina* (Müll. Arg.) Zahlbr.	4	6	4*	4				
266	L	*suspiciosa* (Nyl.) H. Magn.								
267	L	*tenella* (Müll. Arg.) Zahlbr.								402
268	A	*tenuata* (Nyl.) Zahlbr.	4	6	4	3				
269	A	*tenuatula* (Nyl.) Zahlbr.	3	6	3	2				
270	D	*tetraspora* (Nyl.) Oliv.	6	4						
271	D	*tetraspora* (Nyl.) Oliv.	6	5						
272	D	*tetraspora* (Nyl.) Oliv.	6	3						
273	D	*tetraspora* (Nyl.) Oliv.	6	5						
274	A	*thallincola* (Wedd.) Du Rietz	3	6	3	2				
275	A	*tiroliensis* Zahlbr.	5	6	4*	4	5			
276	A	*tiroliensis* Zahlbr.	4	6	3	3				
277	A	*tominii* (Sav.) H. Magn.	4	6	2	1				
278	A	*tornoënsis* H. Magn.	4	6	3	4				
279	A	*trabicola* H. Magn.	3	6	3	3				
280	A	*trachyphylla* (Tuck.) Zahlbr.	4	6	5	4	2			
281	A	*tristiuscula* H. Magn.	4	6	3	3				

TABLE 1—*cont.*

No.	Group	Species	Anthraquinones: Em.	Pa.	Fo., X., Er.	Fa.	Pa-a.	Cl-Em.	Fr.	Other compounds
282	E	*tromsoeënsis* H. Magn.	*4*					6		
283	A	*tucumanensis* H. Magn.	3	6	3	3	1			
284	A	*ulmorum* (Fink) Fink	3	6	3	3				
285	A	*urceolata* B. de Lesd.	3	6	3	3				
286	L	*vacillans* (Th. Fr.) H. Magn.								
287, 288	L	*variabilis* (Pers.) Müll. Arg.								
289	A	*velana* (Mass.) Du Rietz	*3*	*6*	*3**	*3*	1			
290	A	*verruculifera* (Vain.) Zahlbr.	3	6	3	2				
291	A	*vicaria* H. Magn.	*4*	*6*	3	3				
292	F-2	*visianica* (Mass.) Jatta	5	5				6	6	
293	A	*vitellinula* (Nyl.) Oliv.	*4*	*6*	*5**	*5*	2			
294	D	*wrightii* (Tuck.) Fink	*6*	*5*						*Li.*
295, 297	K	*xanthaspis* (Krempelh.)		*4*					*5*	332, *Li.*
298	K	*xanthaspis* (Krempelh.)		4					5	332, *Li.*
299	K	*xanthaspis* (Krempelh.)		3					5	332, Li.
300	K	*xanthaspis* (Krempelh.)		*3*					*5*	332, *Li.*
301	J	*xanthobola* (Krempelh.) Zahlbr.		*4*					*6*	

The numbers refer to the relative amount of anthraquinones present, the most abundant taken as 100%:

6—100–34% 5—33–11% 4—10–3·4%

3—3·3–1·1% 2—1·0–0·34% 1—0·33–0·10%.

Numbers in italics denote that the compound also has been identified by ITLC. Abbreviations: At—atranorin; Cl-Em.—2-chloroemodin; Em.—emodin; Er.—erythroglaucin; Fa.—Fallacinal; Fo.—fallacinol; Fr.—fragilin; Li.—lichexanthone; Pa.—parietin; Pa-a.—parietinic acid; Us.—usnic acid; X.—xanthorin; 332—1-*O*-methylfragilin (compare text); 402—unidentified trichloro compound (compare text). The numbering of the lichens refers to the list of specimens in the Experimental.

* Fallacinol was identified by ITLC. † Xanthorin was identified by ITLC. ‡ Referred to *Pyrenodesmia*. § 28: "*C. fulva* (Schwein.) Steiner". ‖ 72: "*C. phlogina* (Ach.) Flag.". ¶ Referred to *Blastenia*. ** 102: "*C. conjungens* (Nyl.) Zahlbr.". †† 146: "*C. lapicida* (Arn,)". ‡‡ 147–148: "*C. lithophila* H. Magn.". §§ 149: "*C. pyracea* (Ach.) Th. Fr.". ‖‖ 1929, non (B. de Lesd.) Zahlbr. 1931. ¶¶ 186: "*C. irregularis* H. Magn." holotype. *** 190: "*C. havaasii* H. Magn.".

quantitative data were calculated from the heights of the $M^{+\cdot}$ peaks, using correction factors obtained from mass spectra of anthraquinone mixtures with known compositions.

Not only the $M^{+\cdot}$ peaks, but also some peaks from fragment ions have been used for the LMS identifications of compounds (see Experimental). Nevertheless, identifications only by LMS should be regarded as tentative. An example of an LMS (of *Caloplaca cinnamomea*) is shown in Fig. 1. In many cases, the identifications have been verified by "instant thin-layer co-chromatography" (ITLC)[16] with authentic samples (see Table 1).

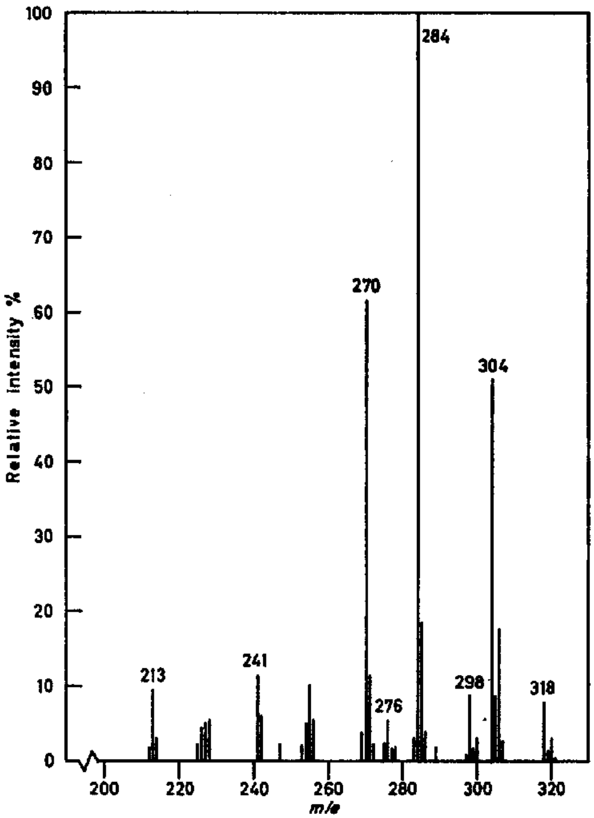


FIG. 1. THE LICHEN MASS SPECTRUM OF *C. cinnamomea* (No. 68).

New Lichen Substances

From *C. xanthaspis*, 1-*O*-methylfragilin (VIII) was isolated by preparative TLC, and identified by comparison (mass spectra) with an authentic specimen, prepared by diazomethane methylation of fragilin.[17a] VIII has not previously been found in Nature, but an isomer, 8-*O*-methylfragilin (IX), occurs in *Nephroma laevigatum* Ach.[17]

[16] The expression ITLC is used as suggested by A. ASZALOS, S. DAVIS and D. FROST, *J. Chromatog.* **37**, 487 (1968).

[17] (a) G. BOHMAN, *Arkiv Kemi* **30**, 217 (1969); (b) G. BENDZ, G. BOHMAN and J. SANTESSON, *Acta Chem. Scand.* **21**, 2889 (1967).

In the LMS of some *Caloplaca* species, a strong peak appears at *m/e* 402 together with satellite peaks at *m/e* 404, 406 and 408, corresponding to a trichloro compound. Since the *m/e* 402 peak (and its satellites) becomes comparatively far stronger at 12 eV than at 70 eV, it is reasonable to assume that it is the $M^{+\cdot}$ peak of an unidentified compound. Although nothing more is known about this compound, it has been included in Table 1, since its distribution within *Caloplaca* might be of interest, once its constitution has been clarified.

"Chemical Grouping" of the Species

The results of the investigation are summarized in Table 1, the origin of the lichen material used being given in the Experimental. Some of the results are not in agreement with the work of Bohman[7] (as regards *C. aurantiaca*, cf. however, Ref. 7b). It has, however, later been found that the sample of *C. percrocata* used by Bohman was misidentified. She found parietinic acid in some species which in the present investigation were found to lack it. However, the occurrence of parietinic acid seems erratic (cf. below) and in e.g. *C. citrina*, *C. congrediens*, *C. microthallina*, *C. murorum* and *C. tiroliensis* it has been found only in some specimens in this investigation.

The investigated species can be arranged in twelve "chemical groups", A–L.

(A) This is the largest of the chemical groups within *Caloplaca*, containing 155 taxa. The major anthraquinone is parietin, accompanied by smaller amounts of emodin, fallacinol, fallacinal, and sometimes parietinic acid. The irregular occurrence of parietinic acid is probably due to the fact that the amounts present in the lichens often are too small to be detected by LMS; hence no significance has been attributed to its absence.

A few subgroups within group A could have been recognized, consisting of species containing unusually large amounts of emodin (e.g. *C. crocina*), fallacinol (e.g. *C. necator*), fallacinal (e.g. *C. altoandina*), and/or parietinic acid (e.g. *C. commixta*). However, since nothing is known about the quantitative regulation of anthraquinone production in lichens, such a subdivision seems premature.

(B) This group is characterized by the presence of usnic acid in addition to most of the anthraquinones present in group A. It consists of only four species: *C. carphinea*, *C. cuyabense*, *C. limitosa*, and *C. stenospora*.

(C) The only species in this group, *C. haematodes*, contains xanthorin as the major anthraquinone, together with most of the "group A pigments".

(D) This group with four members, *C. sibirica*, *C. sinapisperma*, *C. tetraspora*, and *C. wrightii*, has emodin as the main anthraquinone together with smaller amounts of parietin. No other anthraquinones were detected, but the depside atranorin occurs in *C. sibirica* and *C. sinapisperma*, and lichexanthone is present in *C. wrightii*.

(E) This four-membered group (*C. brebissonii*, *C. erythrantha*, *C. subathallina*, and *C. tromsoënsis*) does not contain any 3-*O*-methylated anthraquinones. 2-Chloroemodin dominates and emodin is also present.

(F) Parietin, emodin, 2-chloroemodin, and fragilin are the characteristic compounds of this group. It can be divided in two subgroups: F-1 and F-2. In subgroup F-1, parietin dominates and fallacinol and fallacinal are present. In subgroup F-2, either 2-chloroemodin or fragilin dominates and the presence of fallacinol and fallacinal has not been demonstrated. F-1 contains eight members, F-2 fourteen members.

(G) This group with five members (*C. aurantiaca*, *C. aurea*, *C. chrysophthalma*, *C. flavovirescens* and *C. hokkadensis*) is very similar to group F, but its members lack 7-chloroemodin.

A division similar to that of group F in two subgroups could be possible but, in view of the small number of species involved, it does not seem to be justified.

(H) *C. declarata* and *C. discoidalis* have 2-chloroemodin as the main anthraquinone, together with parietin and emodin. No fragilin could be detected.

(I) In two species 2-chloroemodin and fragilin were found, but no parietin. In contrast to *C. spalatensis*, *C. erythrocarpa* also contains detectable quantities of emodin.

(J) In *C. scabrida* and *C. xanthobola* only the presence of fragilin (dominating) and parietin could be demonstrated. In *C. arizonica* emodin is also present.

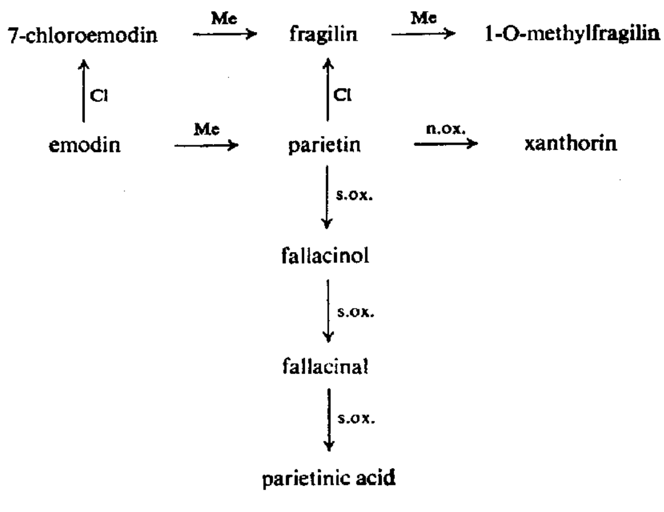
(K) The only member, *C. xanthaspis*, contains parietin, fragilin, and 1-*O*-methylfragilin (VIII). It could be argued that *C. flavovirescens* should be included in this group, since its LMS suggests the presence of small amounts of VIII (or a related compound, e.g. IX). However, VIII could not be detected by ITLC. Since the identity of the minor metabolite thus is uncertain, it is preferred to refer *C. flavovirescens* to group G instead of group K.

(L) In twenty-three taxa, no anthraquinones could be detected. Naturally, it is impossible to demonstrate complete absence, and anthraquinones might be present in at least some of the members of this group, but in too small amounts to allow detection.

Biogenetic and Chemotaxonomical Aspects

The anthraquinones found may be synthesized by the lichens according to Scheme 1. The acetate–malonate origin of emodin in non-lichenized fungi has already been verified,[18] and it may safely be assumed that emodin biosynthesis in lichens follows the same pathway. Some of the transformations leading from emodin to the other anthraquinones have already been postulated by others.[19]

However, the finding of anthrones together with the corresponding anthraquinones in



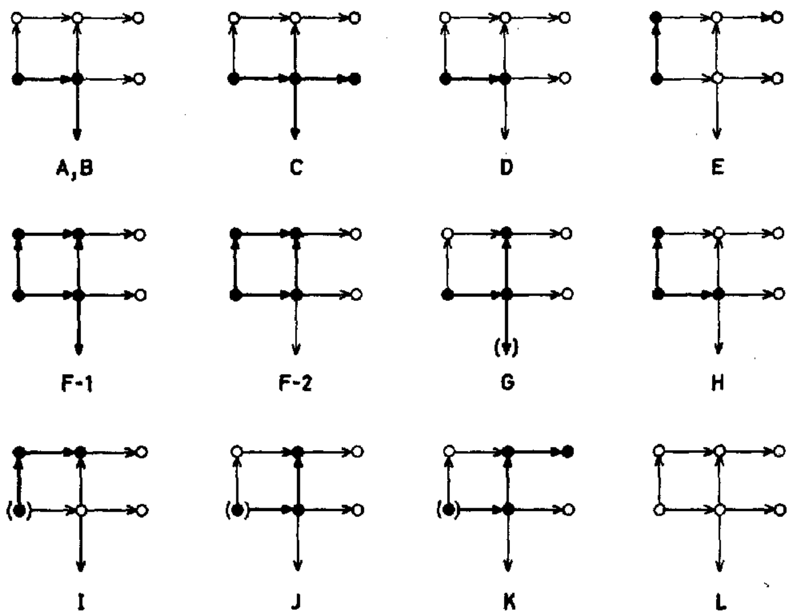
SCHEME 1. SUGGESTED BIOGENETIC RELATIONSHIP BETWEEN THE ANTHRAQUINONES FOUND IN *Caloplaca*. Abbreviations: Cl—chlorination; Me—*O*-methylation; n.ox.—nucleus oxidation; s.ox.—side-chain oxidation.

[18] S. GATENBECK, *Acta Chem. Scand.* **16**, 1053 (1962) and references quoted therein; S. SHIBATA and T. IKEKAWA, *Chem. Pharm. Bull. Tokyo* **11**, 368 (1963).

[19] M. PIATTELLI and M. GUIDICI DE NICOLA, *Phytochem.* **7**, 1183 (1968) and *Ric. Sci.* **38**, 850 (1968); K. MOSBACH, *Angew. Chem. Int. Ed.* **8**, 240 (1969).

some lichens[20] offers the possibility of another interpretation. At least some of the transformations suggested in Scheme 1 might take place at the "anthrone level" and the different anthrones thus formed could be oxidized to the respective anthraquinones. The relationship between the anthraquinones found in *Caloplaca* would be less direct than suggested by Scheme 1—although in principle essentially the same.

The biogenesis of the thirteen "chemical groups" of *Caloplaca* might be summarized as in Scheme 2.



SCHEME 2. POSSIBLE BIOGENETIC RELATIONSHIPS OF THE TWELVE "CHEMICAL GROUPS" OF *Caloplaca*. The circles and arrows represent an abbreviated form of Scheme 1. Heavy lines denote pathways which are probably present; thin lines denote pathways which seem to be absent. Filled circles represent compounds, which have been found (if within parentheses, they have not been found in all members of the group, but are nevertheless probably present). Empty circles represent compounds, the presence of which have not been demonstrated.

Group A is the least interesting, being typical not only of *Caloplaca*, but of most of the lichen genera belonging to Teloschistaceae. Virtually all *Caloplaca* species belonging to sect. *Gasparrinia* are found within group A.

As regards group B, usnic acid has not previously been found together with anthraquinones related to emodin.

Xanthorin (VI),[21] the main pigment of group C, has only once before been found as the main anthraquinone in a lichen: in *Laurera purpurina* (Nyl.) Zahlbr.[22] However, in this case no parietin was found, but instead 1,3,4,8-tetrahydroxy-6-methylanthraquinone. This suggests that in lichens xanthorin may be formed by two alternative pathways.

Compared to group D, group E is of special interest, since it has not been possible to demonstrate the presence of 3-*O*-methylated anthraquinones in this group. From a chemical

[20] I. YOSIOKA, H. YAMAUCHI, K. MORIMOTO and I. KITAGAWA, *J. Jap. Botany* 43, 343 (1968).
[21] W. STEGLICH, W. LÖSEL and W. REININGER, *Tetrahedron Letters* 4719 (1967).
[22] K.-E. STENSIÖ and C. A. WACHTMEISTER, *Acta Chem. Scand.* 23, 144 (1969).

point of view there are two alternatives. The E species can either be regarded as "chemical precursors" of F-2 species or as the result of deficiency mutations of F-2 species.

The group F (with subgroups F-1 and F-2) can be regarded as the chemically most advanced group, the members being able not only to *O*-methylate and chlorinate, but also (in the case of F-1) to oxidise stepwise the methyl side-chain. However, it is not possible to decide whether some of the other groups have evolved from group F, or if group F originates in one of the other groups.

As regards groups G–J, it is not out of the question that these should be regarded as subgroups of group F. The absence of one or two of the compounds I–IV might only be apparent: the amounts could in some cases be below the detection limit of the LMS method.

Group K occupies a very isolated position. No conclusions can be drawn from this singular appearance of 8-*O*-methylfragilin.

The "all negative" group L is probably very heterogeneous in origin. A certain "chemical relationship" to other *Caloplaca* species might be indicated by the occurrence of the unidentified "402" (see above) in a few of the group L species. Furthermore, two group L species contain lichexanthone, which also occurs in some other *Caloplaca.*

The taxonomical implications of some of the present findings will be discussed in a separate paper by Dr. Rolf Santesson.[23]

EXPERIMENTAL

The lichen mass spectra were obtained by the introduction of a small lichen sample into an LKB 9000 gas chromatograph-mass spectrometer via the direct inlet system, as previously described.[14] The temperature of the inlet system was 120–160°, that of the ionization chamber 270–290°, the energy of the ion beam was 70 eV and the electron current was set to 60 μA. Besides the $M^{+\cdot}$ ions, the following fragment ions were used for LMS identifications. (Given are: compound, fragment ion, intensity in % of the corresponding $M^{+\cdot}$ peak.) Anthraquinones: 2-chloroemodin, *m/e* 276, 10%; emodin, *m/e* 213, 8%; fallacinal, *m/e* 297, 8%; fragilin, *m/e* 275, 15%; 1-*O*-methylfragilin, *m/e* 314, 160%; parietin, *m/e* 241, 10%. Other compounds: atranorin, *m/e* 196, 1000%; lichexanthone, *m/e* 257, 30%; usnic acid, *m/e* 233, 200%, *m/e* 260, 110%.

TLC, including preparative TLC, was carried out on Eastman "Chromagram" (6060, silica gel), using solvent systems previously described.[17a,24]

The Lichen Material

Voucher specimens are to be found in the herbarium of Uppsala Botanical Museum (UPS), except for Nos. 295–298, which are to be found in the herbarium of Naturhistoriska Riksmuseet, Stockholm (S). After each number in the list the place of collection, year of collection, reference designation, and—if applicable—holotype, isotype, syntype, or paratype are given.

1: Soviet Union, Jenisejsk, 1876, Brenner. 2: New Zealand, Hew Isl., 1933, Cranwell 261, isotype. 3: Sweden, Gotland, 1918, Magn. 1306. 4: Hawaiian Isl., Necker Isl., 1924, Christophersen 126. 5: U.S.A., New Mexico, 1930, Brouard 21550, isotype. 6: New Zealand, Auckland, Zahlbruckner-Redinger, Lich. exs. 336, isotype. 7: Argentina, Jujuy, 1948, Cabrera L-11. 8: Uruguay, Maldonado, 1948, Osorio 1600. 9: India, United Prov., 1950, Mehra. 10: Sweden, Lycksele L., 1924, Magn. 8106.

11: Uruguay, Maldonado, 1948, Osorio 1586, holotype. 12: Sweden, Jämtland, 1914, Vrang. 13: Austria, Nieder-Österreich, 1912, Baumgartner & Lynge. 14: Czechoslovakia, Moravia, 1920, Suza. 15: Spitsbergen Isl., 1861, Malmgren, syntype. 16: Yugoslavia, Montenegro, 1968, Vězda, Lich. exs. 711. 17: Paraguay, Asuncion, 1893, Malme 1617 B, syntype. 18: U.S.A., S. Dakota, 1961, Wetmore 11227 A. 19: Germany, Wettersteingeb., 1952, Poelt. 20: Germany, Eichstätt, Arnold 273.

21: Germany, Westfalen, 1862, Lahm, syntype. 22: Austria, Krypt. exs. Vind. 1255. 23: Sweden, Jämtland, 1873, Almquist, syntype. 24: Sweden, 1872, Almquist, syntype. 25: Sweden, Medelpad, 1952, R. Sant. 11:4. 26: Sweden, Gotland, 1918, Magn. 2244. 27: France, Indre-et-Loire, 1965, Nordin 3033. 28: U.S.A., "New England", Tuckerman. 29: Sweden, Västergötland, 1948, R. Sant. 30: Sweden, Uppland, 1955, R. Sant. 10785.

[23] R. Santesson, to be published.
[24] J. Santesson, *Acta Chem. Scand.* **21**, 1162 (1967) and *Phytochem.* **9**, 1565 (1970).

31: Sweden, Södermanland, 1898, Malme, Lich. Suec. exs. 103. 32: England, Clonmel, Carroll, Lich. Hibern. exs. 37. 33: England, Cleveland, W. Mudd. 34: Sweden, Uppland, 1965, Nordin 2921. 35: France, Vaucluse, 1957, Clauzade. 36: Yugoslavia, 1876, Głovacki 3808. 37: Spain, Asturias, 1959, R. Sant. 13118e. 38: Austria, Nieder-Österreich, Baumgartner & Lynge, from type loc. 39: U.S.A., Colorado, 1954, Weber S 2306. 40: U.S.A., California, 1957, Shushan S 14755.

41: Paraguay, 1893, Malme, Lich. Herb. Regn. 98. 42: Soviet Union, Taurica, 1910, Mereschkowsky, Lich. Ross. exs. 22, isotype. 43: Mexico, Morelos, 1908, Pringle 15388. 44: England, Scotland, 1969, R. Sant. 20410, holotype. 45: Mexico, Tlalpán, 1925, Amable 197. 46: Galapagos Isl., 1964, Weber L-40205. 47: Germany, Wettersteingeb., 1955, Poelt. 48: no loc., Ex. herb. Ach. 49: England (ex PC), Johnson, N. Engl Lich. Herb. 323. 50: Sweden, Lycksele L., 1924, Magnusson 8097a.

51: U.S.A., California, 1930, Parks 3494. 52: U.S.A., 1882, Green. 53: Hawaiian Isl., Necker Isl., 1924, Christophersen 75b, isotype. 54: U.S.A., S. Carolina, Green, isotype. 55: Spain, Andalusia, 1953, Poelt. 56: Morocco, Rabat, 1934, Werner. 57: Sweden, Östergötland, 1960, Nannfeldt 16252. 58: Sweden, Uppland, 1941, Degelius. 59: France, Haute-Loire, 1954, Clauzade. 60: Sweden, Gotland, 1953, Lindahl.

61: Uruguay, Artigas, 1948, Osorio 1426. 62: Sweden, Uppland, 1959, R. Sant. 13596. 63: Canada, Ontario, 1944, Cain 20261. 64: Uruguay, Maldonado, 1949, Osorio 1919. 65: Brazil, Minas Geraes, 1885, Vainio, Lich. Bras. exs. 1583, syntype. 66: Sweden, Torne L., 1921, Magn. 5885. 67: Sweden, Torne L., 1919, Magn. 3366. 68: Norway, Øst-Finnmark, 1857, Th. M. Fries, syntype. 69: Germany, Eichstätt, 1861, Arnold, Lich. exs. 160. 70: Morocco, Rabat, 1934, Werner.

71: England, Wales, 1964, R. Sant. 16481. 72: Portugal, Estremadura, 1946, Tavares 227. 73: U.S.A., Colorado, 1965, Weber Lich. exs. Colo. 160. 74: Colombia, Lindig. 2601. 75: Norway, Hjerkinn, 1863, Th. M. Fries. 76: Portugal, Alto Alentejo, 1957, Tavares, Lich. Lus. exs. 124. 77: Czechoslovakia, Moravia, 1956, Vězda, Lich. Bohem. exs. 59. 78: Sweden, Torne L., 1967, Hertel 7504. 79: Germany, Eichstätt, 1862, Arnold, Lich. exs. 187. 80: Finland, Utsjoki, 1965, Poelt.

81: Mexico, Baja California, 1963, Weber & McCoy L-36546. 82: Poland, Pieniny Mts., 1956, Tobolewski 194. 83: Paraguay, 1893, Malme, Lich. Herb. Regn. 117a. 84: Hawaiian Isl., Nihoa Isl., 1924, Christophersen. 85: Brazil, Matto Grosso, 1893, Malme 2117 B. 86: Yugoslavia, Dalmatia, 1837, Radlkofer 310. 87: Germany, Niedersachsen, 1959, Ullrich. 88: Italy, Varazze, 1930, Sbarbaro. 89: Brazil, 1885, Vainio, Lich. Bras. exs. 424, syntype. 90: Sweden, Torne L., 1919, Magn. 3102.

91: Brazil, 1894, Malme, Lich. Herb. Regn. 100. 92: Brazil, Pernambuco, 1950, Lamb 5801. 93: Poland, Tatry, 1954, Tobolewski 106. 94: Norway, Tromsø, Norman. 95: U.S.A., S. Dakota, 1960, Wetmore 6443. 96: U.S.A., Massachusetts, Willey. 97: France, Basses-Alpes, 1965, Vězda, Lich. exs. 444. 98: France, Vaucluse, 1951, Clauzade. 99: Norway, Hjerkinn, 1948, Larsson, holotype. 100: Austria, Tirol, 1952, Poelt.

101: Uruguay, Lasellaja, 1946, Lamb 3160. 102: Uruguay, Zahlbr., Lich. exs. 296. 103: Argentina, 1894, Malme, Lich. Herb. Regn. 119. 104: Uruguay, Montevideo, 1947, Osorio 1044. 105: Brazil, Rio de Janeiro, 1885, Vainio, Lich. Bras. exs. 202, syntype. 106: Brazil, Rio Grande do Sul, 1893, Malme 1347. 107: Paraguay, Asuncion, 1893, Malme, Lich. Herb. Regn. 116b. 108: Sweden, Gotland, 1845, Stenhammar. 109: Italy, Puglie, 1948, Degelius. 110: France, Dijon, Persoon, ex. herb. Ach.

111: Sweden, Torne L., 1919, Th. C. E. Fries. 112: Italy, Genova, 1949, Sbarbaro. 113: U.S.A., Wisconsin, 1953, Culberson 3025. 114: Italy, Liguria, Ferrari/Baglietto, isotype. 115: Sweden, Uppland, 1960, R. Sant. 13731. 116: U.S.A., S. Dakota, 1960, Wetmore 7844. 117: Sweden, Västergötland, 1960, Nordin. 118: Brazil, Sao Paulo, 1947, Lamb 5015. 119: Bulgaria, Cepelarska Planina, 1929, Szatala. 120: Sweden, Öland, 1962, R. Sant. 14567b.

121: Sweden, Bohuslän, 1951, Magn. 22624. 122: Norway, Oppland, 1961, R. Sant. 14213. 123: Sweden, Uppland, 1950, Frisendahl. 124: England, Scotland, 1958, Weber & Crundwell S 14292. 125: U.S.A., S. Dakota, 1960, Wetmore 8197. 126: U.S.A., Wisconsin, 1953, Culberson 3021. 127: Brazil, 1885, Vainio, Lich. Bras. exs. 31. 128: Paraguay, 1893, Malme, Lich. Herb. Regn. 118. 129: Soviet Union, Novaja Zemlja, 1921, Lynge. 130: Spitsbergen Isl., 1861, Malmgren, syntype.

131: Spitsbergen Isl., 1861, Malmgren, holotype. 132: Sweden, Jämtland, 1950, Magn. 22059. 133: Sweden, Jämtland, 1910, Malme, isotype. 134: Germany, Rheinpfalz, 1860, Laurer, holotype. 135: Paraguay, Gran Chaco, 1893, Malme. 136: Socotra Isl., Schweinfurth, isotype. 137: South Africa, Cape Prov., 1953, Almborn 502. 138: France, Vaucluse, 1959, Clauzade. 139: South Africa, 1873, De Wylder. 140: South Africa, Cape Prov., 1953, Almborn, Lich. afr. 47.

141: Sweden, Gotland, 1951, R. Sant. 142: Sweden, Västergötland, 1936, Magn. 15262. 143: Portugal, Beira Alta, 1947, Tavares, Lich. Lus. exs. 72. 144: Oceania, Lord Howe's Isl., 1892, Wilson, 145: Sweden, Skåne, 1947, R. Sant. 146: Germany, Eichstätt, Arnold. 147: Sweden, Härjedalen, 1958, R. Sant. 12623a. 148: Greenland, Nugssuaq, 1950, Gelting 13385. 149: England, East Kent, 1961, R. Sant. 15209a. 150: France, Vaucluse, 1965, Vězda, Lich. exs. 374.

151: France, Marseille, Clauzade. 152: Hawaii, 1909, Faurie. 153: Austria, Tyrol, 1958, Poelt, Lich. alp. 62. 154: France, Cap Fréhel, 1954, Clauzade. 155: Soviet Union, Novaja Zemlja, 1921, Lynge, syntype. 156: Czechoslovakia, Moravia, 1920, Suza. 157: Juan Fernandez Isl., 1917, Skottsberg 49, 158: Brazil, Rio de Janeiro, 1885, Vainio, Lich. Bras. exs. 219b, isotype. 159: Sweden, Jämtland, 1912, Malme, isotype. 160: Sweden, Torne L., 1959, R. Sant. 13481a.

161: Soviet Union, Kamtchatka, 1909, Komarov & Savicz 6564/196. 162: Czechoslovakia, 1964, Vězda, Lich. exs. 322. 163: U.S.A. Colorado, 1955, Shushan & Weber S 5271. 164: U.S.A., California, 1874, Eisen, holotype. 165: Sweden, Härjedalen, 1867, Hellbom. 166: Norway, Hordaland, 1916, Du Rietz. 167: Sweden, Torne L., 1927, Vrang. 168: Sweden, Jämtland, 1868, Almquist, holotype. 169: Italy, Spotorno, 1949, Sbarbaro, from type loc. 170: Portugal, Beira Leitoral, 1943, Tavares 161.

171: England, Scilly Isl., 1963, R. Sant. 16108. 172: Sweden, Jämtland, 1914, Magn. 173: U.S.A., Arizona. 1957, Weber & Shushan S 8763. 174: Antarctica, South Georgia, 1902, Skottsberg 15. 175: France, Prevost, 176: Sweden, Lycksele L., 1924, Magn. 7953. 177: Brazil, Minas Geraes, 1892, Malme 267. 178: Sweden, Skåne, 1947, R. Sant. 179: Germany, Eichstätt, 1877, Arnold. 180: Brazil, Matto Grosso, 1894, Malme, isotype.

181: Mexico, 1926, Amable 538, isotype. 182: U.S.A., S. Dakota, 1961, Wetmore 11812. 183: U.S.A., Wisconsin, 1957, Weber & Thomson S 15323. 184: England, Scilly Isl., 1963, R. Sant. 15560. 185: Norway, Vest-Agder, 1953, R. Sant. 186: Norway, Møre, 1947, Magn. 20528. 187: Uruguay, Montevideo, 1947, Osorio 1326, holotype. 188: Sweden, Uppland, 1967, R. Sant. 19141. 189: Sweden, Blekinge, 1964, Nordin 2515. 190: Norway, Hardanger, Havås.

191: South Africa, Cape Prov., v. d. Byl 1024. 192: Greenland, 2te Deutsche Polarfarth, isotype. 193: Brazil, Rio de Janeiro, 1885, Vainio, Lich. Bras. exs. 219, syntype. 194: Brazil, 1892, Malme, Lich. Herb. Regn. 125. 195: Paraguay, Colonia Risso, 1893, Malme 1882 B. 196: France, Vaucluse, 1959, Clauzade. 197: Austria, Krypt. exs. Vind. 766. 198: Sweden, Torne L., 1943, Eriksson. 199: Germany, Wettersteingeb., 1952, Poelt. 200: Sweden, Dalsland, 1938, Magn. 16417.

201: Sweden, Dalsland, 1941, Magn. 17786. 202: Italy, Sicily, 1952, Poelt. 203: England, Derby, Wilson. 204: Juan Fernandez Isl., 1917, Skottsberg 136, holotype. 205: Italy, Anzi, Lich. Lang. 315, isotype. 206: Hawaiian Isl., Necker Isl., 1924, Christophersen 95. 207: Austria, Tyrol, 1958, Poelt, Lich. alp. 77. 208: Brazil, Rio de Janeiro, 1885, Vainio, Lich. Bras. exs. 94. 209: Brazil, Rio de Janeiro, Glaziou 3848. 210: Switzerland, Graubünden, 1967, Vězda, Lich. exs. 650.

211: Chile, Coquimbo, 1917, Skottsberg. 212: Sweden, Torne L., 1921, Magn. 5475. 213: U.S.A., Wisconsin, 1861, Kumlien 23. 214: Hungary, Krypt. exs. Vind. 1880. 215: Italy, 1858, Massalongo. 216: Germany, Ammergauer Berge, 1953, Poelt. 217: Uruguay, Maldonado, 1949, Osorio 1880. 218: U.S.A., 1932, Rapp. 219: Sweden, Östergötland, 1911, Du Rietz. 220: Italy, Liguria, 1948, Sbarbaro, from type loc.

221: South Africa, Cape Prov., 1953, Almborn 1655. 222: Czechoslovakia, 1927, Servit 9607G-31. 223: France, Vaucluse, 1959, Clauzade. 224: Juan Fernandez Isl., 1954, Skottsberg L 38. 225: Argentina, Mendoza, 1903, Malme. 226: Colombia, Lindig. 2614, isotype. 227: Portugal, 1952, Tavares, Lich. Lus. exs. 244. 228: Austria, Tyrol, 1958, Poelt, Lich. alp. 99. 229: Italy, Liguria, 1949, Sbarbaro, isotype. 230: Uruguay, Montevideo, 1949, Osorio 1631, holotype.

231: Yugoslavia, Montenegro, 1929, Servit. 232: Sweden, Bohuslän, 1959, R. Sant. 12925. 233: Sweden, Bohuslän, 1920, Magn. 4849. 234: Sweden, Bohuslän, 1955, Magn. 24596. 235: France, Paris, ex. Herb. Nyl. 29234, fragment of holotype. 236: Juan Fernandez Isl., 1917, Skottsberg. 237: Brazil, Rio de Janeiro, 1885, Vainio, Lich. Bras. exs. 109, isotype. 238: Sweden, Torne L., 1919, Magn. 3278, holotype. 239: U.S.A., Colorado, 1954, Weber S 2309. 240: Sweden, Västergötland, 1940, Magn. 17377.

241: Finland, Karelia, 1870, Norrlin, 242: Sweden, Torne L., 1921, Magn. 5933. 243: Czechoslovakia, Carpatian Mtns., 1968, Vězda, Lich. exs. 715. 244: Italy, Genova, 1947, Sbarbaro 128. 245: U.S.A., 1928, Gray, L 844. 246: Spitsbergen Isl., 1861, Malmgren (in holot. of *C. arctica*). 247: Spitsbergen Isl., 1861, Malmgren, holotype. 248: Italy, Liguria, 1952, Sbarbaro, holotype. 249: U.S.A., California, 1966, Weber, Lich. exs. Colo. 193. 250: Brazil, 1894, Malme, Lich. Herb. Regn. 121.

251: Sweden, Öland, 1912, Du Rietz. 252: Sweden, Gotland, 1944, Pettersson. 253: Sweden, Småland, 1914, Du Rietz. 254: Brazil, Rio Grande do Sul, 1892, Malme 590. 255: Soviet Union, Turkmenistan, 1928, Oxner. 256: France, Pyrénées-Orientales, 1958, Clauzade. 257: Cuba, Wright, Lich. Cubae II, 50, isotype. 258: Falkland Isl., 1907, Skottsberg. 259: France, Haut-Vienne, 1881, Heribaud. 260: South Africa, 1953, Almborn, Lich. afr. 69.

261: Argentina, Jujuy, 1901, R. E. Fries 50. 262: Sweden, Bohuslän, 1952, Magn. 23048. 263: France, Haute-Loire, 1953, Clauzade & Poelt. 264: South Africa, Cape Prov., 1953, Almborn 550. 265: Brazil, Matto Grosso, 1894, Malme. 266: Sweden, Torne L., 1921, Magn. 5560. 267: West Indies, St. Croix, 1927, Evans. 268: France, Vaucluse, 1958, Clauzade. 269: Morocco, 1934, Werner. 270: Norway, Bear Isl., 1868, Th. M. Fries.

271: Spitsbergen Isl., 1928, Lynge. 272: Sweden, Torne L., 1921, Magn. 6234a. 273: Sweden, Torne L., 1919, Magn. 3261. 274: Sweden, Blekinge, 1967, Nordin 4350. 275: Norway, Dovre, 1863, Th. M. Fries. 276: Czechoslovakia, Carpatian Mtns., 1960, Vězda, Lich. exs. 61. 277: Soviet Union, Astrachan, 1926, Savicz, Lich. Ross. 24, isotype. 278: Sweden, Torne L., 1919, Magn. 2907a, holotype. 279: Uruguay, Florida, 1949, Osorio 1752, paratype. 280: U.S.A., Colorado, 1954, Weber S 2384.

281: Sweden, Västergötland, 1919, Magn. 2508, holotype. 282: Norway, Tromsø, Norman, holotype. 283: Argentina, Tucuman, 1945, Digilio-Grassi 2793b, holotype. 284: U.S.A., Wisconsin, 1946, Thomson 2332. 285: U.S.A., New Mexico, 1929, Brouard, isotype. 286: Norway, Finnmark, 1864, Th. M. Fries, holotype. 287: Italy, Lombardia, 1927, Magn. 10686. 288: Sweden, Västergötland, 1934, Magn. 14357. 289: Sweden, Öland, 1867, Zetterstedt. 290: England, Scilly Isl., 1963, R. Sant. 15765.

291: Canada, British Colombia, 1887, Macoun, holotype. 292: Italy, Liguria, Baglietto. 293: U.S.A., S. Dakota, 1960, Wetmore 8904. 294: U.S.A., Texas, Wright 63 bis. 295: Paraguay, Asuncion, 1893, Malme 1435. 296: as 295 but Malme 1649 A6. 297: as 295 but Malme 1649 B6. 298: Paraguay, Paraguari, 1893, Malme, Lich. Herb Regn. 116a. 229: Brazil, Rio de Janeiro, 1885, Vainio, Lich. Bras. exs. 505. 300: Brazil, 1892, Malme, Lich. Herb. Regn. 115. 301: Brazil, Rio Grande do Sul, 1892, Malme 838.

1-O-*methylfragilin* (*VIII*)

C. xanthaspis (samples 295 and 296, about 25 mg of each) were continuously extracted with acetone (2 ml, 24 hr). Preparative TLC (toluene) afforded VIII, identified by comparison (mass spectra) with an authentic sample, also purified by preparative TLC.

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