2 hat im MS ein Molekülion bei *m/e* 460 entsprechend der Summenformel $C_{22}H_{20}O_{11}$. Die Verbindung spaltet fünfmal Keten (42 ME) bis zu einem Ion *m/e* 250 ($C_{12}H_{10}O_6^+$.) ab. Demnach sollte es sich um einen Diphenyläther mit 5 acetylierten OH-Gruppen handeln. **2** ist nach seinem Smp, MS, PMR-, UV- und IR-Spektrum identisch mit dem erstmalig aus *Cystoseira tamariscifolia* isolierten Diphloretholpentaacetat (2,3',4,5',6-Pentaacetoxydiphenyläther [2]).

3 weist einen Molekülpeak *m/e* 502 auf, entsprechend $C_{24}H_{22}O_{12}$ und vermag bis zu sechsmal Keten zu eliminieren bis zu einem Ion $C_{12}H_{10}O_6$ (*m/e* 250). Die bereits nach partieller Ketenabspaltung einsetzende Wassereliminierung, die besonders bei den Endgliedern der Zerfallsreihe zu sehr intensiven Ionen führt: 229 − 18 → 274, 250 − 18 → 232, ist typisch für das zuvor aus *Fucus vesiculosus* isolierte Difucolhexaacetat [3]. **3** stimmt auch in Smp, PMR-, UV- und IR-Spektren mit dieser Verbindung überein.

Die Verbindungen **1**, **2** und **3** stellen Vorstufen der Phlorotannine dar, die normalerweise in typischen 'Physoden' lokalisiert sind. Auch in *Dictyota* sind wiederholt Physoden beobachtet worden [z.B. 4, 5, 6 e.a.]. Überraschenderweise sind Phlorotannine aber nur in verschwindend geringer Menge extrahierber, ausserdem fehlen die sonst immer zu beobachtenden höhermolekularen Dehydropolymerisations-produkte. Die gesammelte *D. dichotoma* epiphytierte auf *Cystoseira baccata*, dir erhebliche Mengen an Phlorotanninen enthält. Es wäre somit denkbar, daß es sich bei den isolierten Substanzen nicht um Stoffwechselprodukte aus *D. dichotoma* sondern um adsorbierte Ausscheidungsprodukte aus *C. baccata* handelt. Dagegen spräche, dass in *C. baccata* zwar Difucol aber kein Diphlorethol, sondern Bifuhalol gefunden wurde [7], das wiederum in *D. dichotoma* fehlt. Unerklärlich bliebe auch, warum nur die Dimerisationsprodukte und keine der zahlreichen höheren Oligomeren aus *C. baccata* von *D. dichotoma* aufgenommen worden sind.

EXPERIMENTELLES

500 g gefriergetrocknete *D. dichotoma* wurden in der zuvor beschriebenen Weise [2] extrahiert und die nach dem Abfiltrieren der lipophilen Anteile mit $CHCl_3$ ausgeschüttelte wäßrige Phase gefriergetrocknet und mit MeOH ausgezogen; Ausbeute 22 g eines methanollöslichen Rohextraktes, der überwiegend aus Mannit besteht. Nach dem Acetylieren wurden die Phenolacetate SC an Kieselgel mit CH_2Cl_2–Me_2CO (49:1) angereichert und durch wiederholte DC an Kieselgel F_{254}—Platten (Merck, 0,25 mm) mit $CHCl_3$–Me_2CO (47:3) vom restlichen Mannitacetat abgetrennt. Die interessierenden Zonen wurden ausgekratzt, mit $CHCl_3$, Me_2CO mehrmals eluiert und zuletzt aus MeOH umkristallisiert. Insgesamt wurden 22 kg gefriergetrocknete Algen extrahiert und ergaben: *Phloroglucintriacetat* (**1**), R_f 0, 0,59, Ausb.: 4,5 mg, Smp 105–107°, *Diphloretholpentaacetat* (**2**), R_f 0, 53, Ausb.: 11,2 mg. Smp 112–114°. (MeOH) (Lit. [2] 113–114°). *Difucolhexaacetat* (**3**), R_f 0, 49, Ausb.: 7,4 mg, Smp 177–178°. (Lit. [8] 177–178°).

Anerkennungen—Wir danken der DFG für eine Sachbeihilfe, Frl. Koch für die Aufnahme der NMR-Spektren, den Herren Proff. Günther und Vogel für die Möglichkeit, auf dem ihnen von der DFG zur Verfügung gestellten Gerät messen zu können und der Station Biologique de Roscoff für einen Arbeitsplatz zur Sammlung der Algen.

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DIHYDROCHALCONES FROM *VIBURNUM DAVIDII* AND *V. LANTANOIDES*

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Key Word Index—*Viburnum davidii*; *V. lantanoides*; Caprifoliaceae; dihydrochalcones; davidioside; davidigenin; 4'-*O*-methyldavidioside; 4'-*O*-methyldavidigenin; ^{13}C-NMR.

INTRODUCTION

Known dihydrochalcones from natural sources are few and of sporadic occurrence. Williams, in a review [1]. presented a list of 5 glycosides and two free dihydrochalcones from 5 plant families: Hemionitidaceae (ferns), Liliaceae, Salicaceae, Rosaceae and Ericaceae (angiosperms).

From *Viburnum davidii* (Caprifoliaceae) Bohm and Glennie [2] isolated the glucoside (**1**), characterized by hydrolysis to glucose and 2',4,4'-trihydroxydihydrochalcone (**2**). For **1**, only UV-data were given, proving that glucose was attached to the 2'-oxygen.

RESULTS AND DISCUSSION

From leaves of *V. davidii* Franch., we have isolated **1** and the corresponding aglucone **2**, for which we

*In agreement with B. A. Bohm, University of British Columbia, Canada (ref. 2).

propose the names davidioside* and davidigenin, respectively. In addition, a third dihydrochalcone, 4′-*O*-methyldavidigenin (**5**), was found. Its PMR spectrum (Table 1) was similar to that of **2**, but showed also the presence of an O-Me group at 3.85 ppm. The corresponding diacetate **6** exhibited a downfield shift for the protons of the B-ring. In the UV-spectrum of **5**, a bathochromic shift was produced by addition of $AlCl_3$. Hence, the OH-groups must be situated at the 2′- and 4-positions, leaving the 4′-position for the OMe group, a conclusion substantiated by comparison with synthetic 2′,4-dihydroxy-4′-methoxydihydrochalcone. Leaves of *V. lantanoides* afforded the two glucosides, davidioside (**1**) and 4′-*O*-Me davidioside (**3**); **3** after acid hydrolysis gave **5**. Contrary to **5**, **3** showed no shift in UV by the addition of $AlCl_3$. Therefore glucose is attached to the 2′-oxygen of **3**.

Evidence for the β-glucopyranoside unit in **1** and **3** was provided by the ^{13}C NMR-spectra. ^{13}C NMR-data for a variety of flavonoid compounds, including chalcones, have been published [3]. We present data for the dihydrochalcones of the present study and for some model compounds (Table 2). The spectrum of davidigenin (**2**) was assigned by comparison with the published spectrum [3] of isoliquiritigenin, the chalcone corresponding to **2**. Likewise, the spectrum of 4-*O*-methyldavidigenin (**5**) was assigned by comparison with that of **9**. Only small shift differences were observed between a chalcone and the corresponding dihydrochalcone, except for C-1, C-4, C-α and C-β. The large difference between the C=O shift of **2** (200.7 ppm) and isoliquiritigenin (191.4 ppm in DMSO) may be ascribed to the different solvents used, as no such difference is seen between the C=O signals of **5** and **9**. The spectra of the glucosides **1** and **3** were assigned by comparison with the corresponding genins **2** and **5**, using the model compounds peonol β-D-glucopyranoside (**8**) and peonol (**7**). In these pairs of 2′-glucosides/genins, shift differences of more than 3 ppm were found for C-α(*ca* 5.5 ppm), C=O (*ca* 3.5 ppm), *C-1 (*ca* 7.5 ppm) and C-2 (*ca* −6.5 ppm).

The absorptions from the glucopyranoside moiety of the 4 glucosides in the present study follow closely the values found for iridoid glucosides [4]. Thus, the shifts of C-2″—C-6″ all fall within 0.4 ppm of the mean values, regardless of the aglucone. The shift value for an anomeric carbon atom, however, appears to be more sensitive to the nature of the aglucone. This consistency in the spectra of β-glucopyranosides provides a convenient way of determining their identity in a nondestructive way.

* For the pair **8**/**7** the difference is −0.3 ppm.

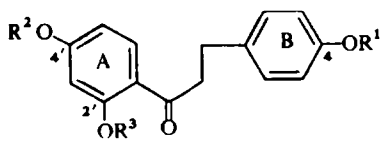
EXPERIMENTAL

General procedures were as earlier described [4,5]. Microanalyses were performed at NOVO Microanalytical Laboratory, Bagsværd, Denmark. *V. davidii* foliage was collected in July at the Botanical Garden of The University of Copenhagen. A voucher (IOK-22/75) has been deposited at the Botanical Museum. *V. lantanoides* was collected in October at the Royal Botanic Gardens, Kew, England, (catalogue no. 291-59-29103).

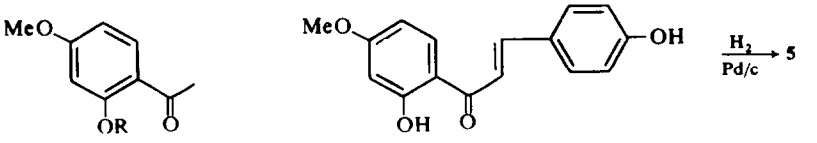
V. davidii. Frozen leaves (270 g, kept at −23°) were extracted with EtOH and worked up as earlier described [5] to give a mixture of glycosides (13.2 g). The mixture (4.3 g) was chromatographed on a column of Si gel (450 g) and eluted with $CHCl_3$–MeOH (8:1, 6:1, and 4:1). The first fraction (425 mg, 0.48%) consisted of **5**. It was crystallized from H_2O–MeOH (4:1), mp 75–77°; λ_{max}^{MeOH} nm (log ε): 213(4.31), 216 *sh* (4.30), 226*sh* (4.16), 236 *sh* (3.91), 276(4.18), 317(3.82); $AlCl_3$ added: 225, 242 *sh*, 305, 360. (Found: C, 68.38; H, 6.02. $C_{16}H_{16}O_4$, 0.5 H_2O requires: C, 68.33; H, 6.11). Fraction 2 (560 mg, 0.64%) containing **2** was crystallized as above, mp 155.5–156° (lit. [2]: 158–160°); λ_{max}^{MeOH} nm (log ε); 213(4.41), 217 *sh* (4.39), 226 *sh* (4.23), 238 *sh* (3.97), 278(4.22), 317(3.94); $AlCl_3$ added: 222, 244 *sh*, 308, 362 (lit. [2]: λ_{max}^{EtOH} nm: 278, 314; $AlCl_3$: 306, 356). Fraction 3 (160 mg, 0.18%) consisted of **1**, identical to the sample below (PMR, TLC).

V. lantanoides. Dry powdered leaves (39 g) were eluted with EtOAc in a Soxhlet apparatus for 20 hr. The EtOAc soln was extracted with H_2O, which was then evapd to dryness (3.7 g). Chromatography on Si gel as above, provided a first fraction consisting of **3** (600 mg, 1.5%), which was crystallized from EtOH–H_2O (3:1), mp 182–182.5°. λ_{max}^{MeOH} nm (log ε): 213(4.31), 224(4.36), 268(4.15), 286 *sh* (3.96), 299 *sh* (3.83); no changes on addition of $AlCl_3$. $[\alpha]_D^{22}$ −71° (MeOH; *c* 0.6). (Found: C, 60.71; H, 6.07. $C_{22}H_{26}O_9$ requires C, 60.82; H, 6.03). The second fraction (1240 mg, 3.2%), after preparative TLC, gave **1** as a syrup. λ_{max}^{MeOH} nm (log ε): 210(4.31), 225(4.31); 270(4.10), 287(3.95), 300(3.84); $AlCl_3$: no change. (lit. [2]: λ_{max}^{EtOH} nm: 278, 314; $AlCl_3$: no change). $[\alpha]_D^{22}$ −59° (MeOH; *c* 0.5). (Found: C, 55.30; H, 6.20. $C_{21}H_{24}O_9$, $2H_2O$ requires: C, 55.26; H, 6.20).

Acetylation of **3** yielded the pentaacetate **4** which was crystallized from EtOH, mp 107.5–108°; $[\alpha]_D^{22}$ −54° ($CHCl_3$; *c* 0.4). (Found: C, 59.50; H, 5.68. $C_{32}H_{36}O_{14}$ requires: C, 59.62; H, 5.63).



1: $R^1 = R^2 = H$; R^3 = Glc
2: $R^1 = R^2 = R^3 = H$
3: $R^1 = H$; R^2 = Me; R^3 = Glc
4: R^1 = Ac; R^2 = Me; R^3 = $GlcAc_4$
5: $R^1 = R^3 = H$; R^2 = Me
6: $R^1 = R^3$ = Ac; R^2 = Me



7: R = H
8: R = Glc

Table 1. PMR data for dihydrochalcones

Compound	$H_{2,6}$	$H_{3,5}$	H_α	H_β	$H_{3'}$	$H_{5'}$	$H_{6'}$	OMe	$H_{1''}$
1	7.09	6.73	3.28	2.87	6.80	6.56	7.64	—	5.01
2	7.22	6.83	3.21	2.95	6.39	6.47	7.79	—	—
3	7.06	6.72	3.34	2.84	6.89	6.67	7.66	3.84	5.13
4	7.26	7.00	3.17	3.01	6.60	6.64	7.78	3.85	—
5	7.12	6.76	3.26	2.90	6.44	6.49	7.92	3.85	—
6	7.33	7.09	3.24	2.94	6.76	6.82	7.99	3.89	—

Solvent: d_6-acetone (except for 4 ($CDCl_3$)); standard TMS; shift values in ppm ±.02.

Table 2. ^{13}C-NMR data of dihydrochalcones and model compounds*

Compound	C_1	C_2	C_3	C_4	C_β	C_α	$C_{C=O}$	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	$C_{1''}$	$C_{2''}$	$C_{3''}$	$C_{4''}$	$C_{5''}$	$C_{6''}$	OMe
1	133.8	130.4	116.1	154.4	30.2	44 7	204.7	121.2	158.7	104.0	162.6	111.0	133.3	101 3	73.8	76.7†	70.3	77.1†	61.6	
2	132.1	129.6	115.4	155.8	29.5	39.7	200.7	113.3	165.6†	103.0	164.7†	108.1	133.0							
3	133.0	129.5	115.4	154.8	29.9	45.1	203.1	121.9	158.7	102.1	165.1	108.7	132.1	101.5	73.9	77.3	70.4	77 3	61.6	55.5
5	131 7	129 3	115 1	155.6	29.2	39.5	200.1	114 6	165.3†	100.7	166.1†	107.1	132.2							55.1
7						26.2	203 5	114.4	165.8†	101.3	166.8†	107.7	133.4							55.7
8						31.8	203.0	121.5	159.2	102.3†	165 3	109.3	133.2	101.1†	73.8	76.9†	70.4	77.2†	61.6	56.5
9	126.9	131.2	116.1	160.4	144.8	117 6	201 0	114.3	166.4†	101.1	166.9†	107.4	132.0							
salidro side	131.1	131.1	116.2	154 8	35.2	71.8								103 1	74.0	76 7	70.5	76.7	61.6	

*Solvent/standard: D_2O/dioxan, (glucosides); d_6-acetone/TMS.
†Numbers intechangeable in same horizontal row.

Hydrolysis of **3** (40 mg) in 2N HCl (5 ml) gave, after extraction with Et_2O, **5**, mp 70–72°, identical to the sample above.

Synthesis of **5**. 2',4-Dihydroxy-4'-methoxychalcone (**9**) was prepared as described [6]. Hydrogenation (atm. pres.) of **9** (160 mg) in EtOH with 5% Pd/C (20 mg) gave **5**, identical (mp, mmp. PMR) to the other samples.

Acetylation of **5** afforded the diacetate **6**, which was crystallized from EtOH, mp 81–82°. (Found C, 67.36; H, 5.60. $C_{20}H_{20}O_6$ requires C, 67.40; H, 5.66).

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1,3,6-TRIHYDROXY-7-METHOXY-8-(3,7-DIMETHYL-2,6-OCTADIENYL)XANTHONE FROM *GARCINIA COWA*

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Key Word Index—*Garcinia cowa*; Guttiferae; 1,3,6-trihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienyl)xanthone; structural determination.

Abstract—1,3,6-Trihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienylxanthone has been isolated from the stems of *Garcinia cowa*.

Although a 3-methyl-2-butenyl (prenyl) substituent has been found in a number of xanthones from the families *Guttiferae* and *Moraceae*, xanthones containing an unmodified 3,7-dimethyl-2,6-octadienyl (geranyl) side-chain