to give the diacetate (**2**, 11.6 mg). Mp 188–193°, lit. 193–195° [2] 190–192° [3]; $[\alpha]_D^{20}$ +13.5 ($CHCl_3$, *c* 0.89), lit. 21.2° [MeOH–$CHCl_3$] (1:1), *c* 0.5] [3]; FDMS *m/z* (rel. int.): 419 $[M+H]^+$ (23), 358 $[M-AcOH]^+$ (100); EIMS *m/z* (rel. int.): 403 $[M-Me]^+$ (0.4), 358 (31), 300 (13), 255 (24), 43 (100); IR-ν_{max}^{KBr} cm^{-1}: 1740, 1720; ^1H NMR (270 MHz, $CDCl_3$: 0.83 (3H, *s*, H_3-19), 1.02 (3H, *s*, H_3-18), 2.01 (3H, *s*, Ac), 2.02 (3H, *s*, Ac), 2.07 (3H, *s*, H_3-21), 2.38 (1H, *d*, *J* = 7.5 Hz, H-17), 2.41 (1H, *ddd*, *J* = 7.5, 7.5, 13.5 Hz, H-15a), 4.68 (1H, *m*, H-3), 5.49 (1H, *ddd*, *J* = 4.4, 7.5, 7.5 Hz, H-16).

$LiAlH_4$ *reduction of* **3** *to yield compound* **4**. To a soln of **3** (8 mg) in THF (0.5 ml), $LiAlH_4$ (2 mg) was added and the soln was stirred for 3 hr at room temp. After extraction with Et_2O, the product was purified on a silica gel column [MeOH–$CHCl_3$ (3:97)] to give **4** as a solid (3 mg). EIMS *m/z* (rel. int.): 351 $[M-Me]^+$ (0.8), 335 $[M-CH_2OH]^+$ (27), 317 (14), 299 (26); ^1H NMR [270 MHz, CD_3OD–$CDCl_3$ (1:1), TMS]: 0.84 (3H, *s*, H_3-19), 1.09 (3H, *s*, H_3-18), 1.42 (3H, *s*, H_3-21), 2.22 (1H, *m*, H-15a), 3.45–3.80 (2H, *m*, H_2-22 and 1H, *m*, H-3).

$NaIO_4$ *oxidation of* **4** *to yield compound* **1**. To a soln of **4** (4 mg) in dioxane (0.8 ml), $NaIO_4$ (10 mg) in H_2O (0.1 ml) was added. The mixture was kept overnight at room temp. After extraction with EtOAc the product was purified on a silica gel column eluted with MeOH–$CHCl_3$ (1:19) affording an oxidation product which was shown to be identical with the isolated material **1** (mp, $[\alpha]_D$, TLC, ^1H NMR, EIMS).

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A GLYCOSIDE FROM DRIED ROOTS OF *CYNANCHUM PANICULATUM*

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Key Word Index—*Cynanchum paniculatum*; Asclepiadaceae; neocynpnoside A; 13,14:14,15 disecopregnane dilactone; deoxysugar.

Abstract—A new glycoside, neocynapanoside A, of disecopregnane with five-and nine-membered lactone rings was isolated from a Chinese herbal drug 'Xu-Chang-Qing' which is the dried roots of *Cynanchum paniculatum*. The structure of the aglycone was deduced to be 15,20α:18,20β-diepoxy-13,14:14,15-disecopregna-5,12-dien-14(16), 18(20β)dioic acid dilactone as found in neocynapanogenin A. The total structure of the new glycoside was established as neocynapanogenin A 3-α-L-cymaropyranosyl-(1 → 4)-β-D-digitoxopyranosyl-(1 → 4)-β-D-oleandropyranoside.

INTRODUCTION

The Chinese herbal drug 'Xu-Chaung-Qing' which is the dried root of *C. paniculatum* Kitagawa has been used as an anodyne and for the therapy of chronic tracheitis in northern China [1]. It possess a peculiar odour due to paeonol which is the odorous principle of this plant [2]. In our recent investigations, several disecopregnane glycosides (cynapanosides A, B, and C) have been isolated and their structures determined [3] in addition to the separation of known cynatratoside B [4] and 14β-hydroxy pregnenolone [5]. We wish to describe in this paper the isolation and structure determination of a new glycoside, neocynapanoside A (**1**) from a glycoside fraction of the drug.

*Part 69 in the series 'Studies on the Constituents of Asclepiadaceae Plants'. For part 68 see Hayashi, K., Iida, I., Nakao, Y. and Kaneko, K. (1988) *Phytochemistry* (in press).

RESULTS AND DISCUSSION

Neocynapanoside A **(1)** had the molecular formula $C_{41}H_{60}O_{16}$ by FDMS (M^+ at m/z 808) and ^{13}C NMR spectrometry. The carbon chemical shifts due to the sugar chain of **1** coincided with those of cynapanoside B **(3)** and atratoside B **(4)** which have terminal α-cymaropyranosyl, β-digitoxopyranosyl, and β-oleandropyranosyl groups [3, 4]. The fragment peaks at m/z 663[M − 144 − H]$^+$, 533[663 − 130]$^+$, and 386[533 − 144]$^+$ in the FD mass spectrum of **1** indicated the stepwise cleavage of each sugar unit from the chain. Therefore, the second sugar in the chain was deduced to be digitoxose. These facts and the chemotaxonomical analogy with the coexsisting **3** and **4** suggested that the order of the sugar sequence was α-L-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-oleandropyraonse.

The elemental compositon corresponding to the aglycone moiety, which was tentatively named as neocynapanogenin **A(2)**, was calculated as $C_{21}H_{26}O_7$. This carbon number suggested that the aglycone was a pregnane derivative as found in other asclepiadaceous aglycones. Two olefinic bonds and two ester or lactone carbonyl groups were verified from the ^{13}C NMR spectrum. IR absorptions at 1750 and 1660 cm^{-1} were ascribable to an α,β-unsaturated five-membered lactone which was supported by UV absorption at 230 nm (ε 5500). The other carbonyl group was assignable to a nine-membered lactone (1715 cm^{-1}) similar to that of other known glaucogenin type aglycones [6]. On comparison of the ^{13}C NMR spectra of **1** and **3**, the chemical shifts for the carbons of the aglycone moieties, gave signals from C-1 to C-10 which were almost identical with each other. The proton–proton COSY spectrum of **1** suggested a correlation of the proton signals from an olefinic proton at δ 5.77 (*br t*, J = 1.0 Hz, H-6)→a hydroxymethine proton at 4.94 (*dt*, J = 8.8, 1.0 Hz, Hα-7)→ a methine at 2.85 (*dd*, J = 11.7, 8.8 Hz, Hβ-8)→ a methine at 2.30 (*ddd*, J = 12.2, 11.7, 6.2 Hz, Hα-9)→ a methylene at 2.34 (*m*, Hα-11) and 4.24 (*q*, J = 12.2 Hz, Hβ-11)→ a β-proton of the α,β-unsaturated lactone at 6.23 (*dd*, J = 12.2, 4.4 Hz, H-12). A coupling network from δ 3.59 (*d*) to 3.99 (*dd*) and 4.31(*dd*) via 5.82 (*ddd*) was assignable to the protons from Hα-17 to Hα,β-15 via Hα-16 respectively. The ^1H and ^{13}C hetero nuclear COSY spectrum confirmed the assignments of ^1H and ^{13}C NMR signals as shown in Tables 1 and 2. The lower field shift of the signal of the 11β-proton at δ 4.24 was affected by the anisotropic effect of the carbonyl group of the five-membered lactone; on the other hand the 11α-proton resonated normally at 2.34. These results lead to the conclusion that **1** is neocynapanogenin A 3-*O*-α-L-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-oleandropyranoside. Biogenetically, the glaucogenin type aglycone was converted to a neocynapanogenin A type aglycone by oxidation at the C-18 position.

EXPERIMENTAL

Mps: uncorr. The ^1H NMR spectra were run at 100, 270 and 400 MHz spectrometers in $CDCl_3$ or C_5D_5N soln with TMS as int.standard; ^{13}C NMR spectra on a JEOL FX-90Q spectrometer in C_5D_5N. Optical rotations were measured with a JASCO DIP-4 digital polarimeter at room temp. UV spectra were obtained in MeOH. CC were carried out on Wakogel C-100, C-200, and C-300 for normal phase, and Fujigel ODS Q-3 for

Table 1. ^1H and ^{13}C NMR chemical shifts of the aglycone moiety of compound **1**

C	δ_C	δ_H[multiplicity, J (Hz)]
1	37.1	1.20 (*m*), 1.75 (*m*)
2	30.2	2.02 (*br d*, 13.0), 1.25 (*m*)
3	76.9	3.81 (*tt*, 11.2, 4.4)
4	38.8	2.63 (*ddd*, 13.4, 4.4, 1.6), 2.34–2.47*
5	141.3	
6	126.9	5.77 (*br t*, 1.0)
7	71.0	4.94 (*dt*, 8.8, 1.0)
8	51.2	2.85 (*dd*, 11.7, 8.8)
9	51.5	2.30 (*ddd*, 12.2, 11.7, 6.2)
10	38.8	
11	27.1	2.34–2.47*, 4.24 (*q*, 12.2)
12	146.3	6.23 (*dd*, 12.2, 4.4)
13	130.0	
14	179.0	
15	71.1	4.31 (*dd*, 10.3, 7.3), 3.99 (*dd*, 10.3, 4.9)
16	76.9	5.82 (*ddd*, 7.8, 7.3, 4.9)
17	54.4	3.59 (*d*, 7.8)
18	167.4	
19	19.9	1.15 (*s*)
20	113.3	
21	23.4	1.65 (*s*)

δ values (ppm) from internal TMS in C_5D_5N.

*Overlapping with other signals.

When two proton signals in a row, the former is an α-proton, the latter is a β-.

Table 2. ^1H and ^{13}C NMR chemical shifts of the sugar moiety of compound **1**

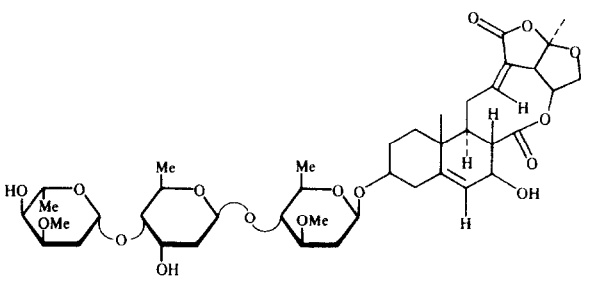
C	δ_C	δ_H
Ole-1	98.1	4.8 (*dd*, 9.9, 1.9)
2	37.9	1.8, 2.34–2.47[a]
3	79.2	3.55[b]
4	83.1	3.55[b]
5	71.7	3.55[b]
6	18.8	1.39 (*d*, 6.3)
3-OMe	57.4	3.39 (*s*)
Dgt-1	98.5	5.44 (*dd*, 9.8, 1.7)
2	38.4	2.34–2.44[a], 1.94 (*ddd*, 13.3, 9.8, 2.9)
3	67.9	4.14 (*m*)[c]
4	80.8	3.45 (*dd*, 9.3, 2.9)
5	69.2	4.14 (*dq*, 9.3, 5.9)
6	18.4	1.44 (*d*, 5.9)
Cym-1	98.4	5.08 (*dd*, 9.8, 1.7)
2	32.3	1.9, 2.34–2.44[a],
3	76.6	3.72 (*ddd*, 4.4, 4.4, 44.4)
4	72.8	3.62 (*dd*, 8.8, 4.4)
5	67.1	4.47 (*m*)
6	18.6	1.45 (*d*, 6.4)
3-OMe	56.8	3.55 (*s*)

δ values (ppm) from internal TMS in C_5D_5N.

[a–c] Overlapping with each other.

When two proton signals in a row, the former is an α-proton, the latter is a β-.

Ole, oleandrose; Dgt, digitoxose, Cym, cymarose.



1

reversed phase. TLC was carried out on precoated plates of Kieselgel $60F_{254}$ (Merck). Abreviations are used for sugars in this section as follows: cym, cymarose; dgt, digitoxose; ole, oleandrose.

Plant material. Xu-Chang-Qing used in this research was obtained in a Formosan market and identified by Dr. Hong-Yen Hsu (Brion Research Institute of Taiwan).

Isolation of neocynapanoside A (**1**). The extraction and isolation processes were the same as those described in the previous report [3]. The CC fr which gave cynapanoside B (**3**, 26.8 mg) afforded 19.7 mg of neocynapanoside A (**1**) by further prep. HPLC separation (Waters 45 type pump; column, Toyo Soda TSK gel ODS-80TM 4.6 mm i.d. × 25 cm, 5μ).

Neocynapanoside A. Amorphous white powder (mp 105–108°), $[\alpha]_D$ −57.3° ($CHCl_3$; *c* 1.54). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1750 (C=O of five-membered lactone), 1715 (C=O, nine-membered lactone), 1660 (C=C of α,β-unsaturated five-membered lactone). UV λ_{max}^{EtOH} nm (ε): 209 (4800), 230 (5,500). FD MS *m/z*: 847[M+K]$^+$, 831[M+Na]$^+$, 808[M]$^+$, 663[M−144−H]$^+$, 533 [663−130]$^+$, 389 [533−144]$^+$. ^{1}H and ^{13}C NMR are shown in Tables 1 and 2.

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A SUBSTITUTED CINNAMOYL ESTER FROM *CLEISTOPHOLIS STAUDTII*

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Key Word Index—*Cleistopholis staudtii*; Annonaceae; Cleistophostaudin; 3-hydroxy-1,7,7-trimethylbicyclo [2.2.1]heptanyl-(*trans*)-4-hydroxy-3-methoxy cinnamate; methyl-(*trans*)-(*trans*)-10,11-dihydroxyfarnesoate.

Abstract—Cleistophostaudin, the novel ester, 3-hydroxy-1,7,7-trimethyl bicyclo[2.2.1]heptanyl-(*trans*)-4-hydroxy-3-methoxycinnamate was isolated from the stem bark of *Cleistopholis staudtii*, and its structure determined by spectroscopic data and degradative studies. The previously known methyl-(*trans*)-(*trans*)-10,11-dihydroxyfarnesoate was also isolated from the same source.

INTRODUCTION

The genus *Cleistopholis* (Engl. & Pierre) is widely known in the tropical forest zone of west and central Africa [1] for its folkloric application against a number of ailments such as tuberculosis, bronchitis, dysentery, whitlow and oedema [2]. Previous studies on the genus report [3–5] the isolation of alkaloids, sesquiterpenes and phenylpropenes. As part of our contribution to the study of the genus, we report herein the isolation and characterization of a novel substituted cinnamic acid ester (**1**) along with an acyclic farnesoic acid methyl ester (**2**) from *C. staudtii*