gel permeation on Sephadex LH-20. Sugar [3,4] and methylation [5] analyses showed **3** and **4** to be glucopyranosides. The structure of **3** is evident from its elemental composition, spectral properties and the fact that it gave *p*-cresyl-β-D-glucopyranoside upon catalytic hydrogenation. Parishin (**4**) is a neutral substance which on catalytic hydrogenation followed by treatment with diazomethane yielded *p*-cresyl-β-D-glucopyranoside and trimethyl citrate in the molar ratio 3:1. The fission must be due to hydrogenolysis of benzyl esters, as no signals for aromatic methyl groups were observed in the NMR spectrum of **4**. These results demonstrate that **4** is tris[4-(β-D-glucopyranosyloxy)benzyl] citrate, a structure also consistent with the NMR spectrum.

EXPERIMENTAL

General conditions were the same as in an earlier communication [2].

Plant material. Vanda parishii. Rchb.f. was delivered from Mr N. Prakash, Chandra Orchid and Bulb Nurseries, 8 1/2 miles P.O. Kalimpong, West Bengal, India.

Isolation of **3** *and* **4**. Fresh plants of *V. parishii* (3 kg) were extracted with MeOH (10 l), and the solution was concentrated to 0.65 l. A part (100 ml) of this extract was diluted to 300 ml with water and washed with $CHCl_3$ (4 × 50 ml). The aqueous layer was saturated with butanol and extracted with butanol saturated with water (7 × 50 ml). The butanolic phase was washed with water (25 ml) and evaporated to dryness. A part (2 g) of the residue (6.4 g) was chromatographed on a silica gel column (5 × 8.5 cm) using $CHCl_3$–MeOH–H_2O (13:7:2, lower phase) as eluent. The fraction containing **3** (300 mg) was filtered through a column of Sephadex LH-20 (5 × 70 cm) using EtOH–H_2O (1:1) as eluent giving crude **3** (96 mg), which was crystallised from *iso*-PrOH–H_2O. Recrystallisation from EtOAc–EtOH gave **3** (56 mg). A part (220 mg) of the fraction containing **4** (450 mg) was chromatographed on silica gel (2.6 × 11 cm) using the same eluent as above. The fraction containing **4** (150 mg) was filtered through a column of Sephadex LH-20 (2.5 × 83 cm) using EtOH–H_2O (1:1) as eluent, giving **4** as a colourless amorphous solid (78 mg).

Glucoside **3**. Needles (EtOAc–EtOH), mp 154–157°C; $[\alpha]_{578}^{22}$ − 63° (*c* 0.77, MeOH). (Found: C 54.6; H 6.3; O 39.1. $C_{13}H_{18}O_7$ requires: C 54.5; H 6.3; O 39.1). IR: ν_{max}^{KBr} 3700–3000(*s*), 1615(*m*), 1590(*m*), 1510(s) cm^{-1}. UV: λ_{max}^{MeOH} (log ε) 277.5 (2.96), 271 (3.04) nm. ^1H NMR (D_2O): δ 3.36–4.12 7.19 and 7.42 (4 H, A_2B_2 system, *J* 9 Hz).

Parishin (**4**). Amorphous solid, $[\alpha]_{578}^{22}$ −59° (*c* 0.80, MeOH). IR: ν_{max}^{KBr} 3700–3000(*s*), 1735(*s*), 1615(*m*), 1590(*m*), 1515(*s*) cm^{-1}. ^1H NMR (D_2O): δ 2.76 and 2.94 (4 H, two AB systems, *J* 15 Hz), 3.4–4.0 (18 H), 4.4–5.1 (the benzylic and the anomeric protons; the HOD signal partially overlapping), 6.9–7.4 (12 H). ^1H NMR (Pyridine-d_5): δ 3.32 and 3.37 (4 H, two AB systems, *J* 15 Hz), 3.80–4.66 (18 H), 5.09 (*s*, 4 H), 5.28 (*s*, 2 H), 5.58 (*d*, 3 H, *J* 6 Hz), 7.1–7.5 (12 H).

Hydrogenation of **3**. A soln of **3** (51 mg) in MeOH (9 ml) was hydrogenated over Pd (20 mg, 10% on carbon) at room temp. and atm. pres. After 7 hr the catalyst was filtered off and the soln was evaporated to dryness giving *p*-cresyl-β-D-glucopyranoside, mp 180–182°C (*iso*-PrOH–H_2O); $[\alpha]_D^{22}$ −67° (*c* 0.76, H_2O) (lit. [6] mp 178–179.5°C; $[\alpha]_D^{20}$ − 67.7° (H_2O)), further identified by NMR.

Hydrogenation of **4**. Parishin (92 mg) was hydrogenated as described for **3**. Catalyst was filtered off and the soln was treated with an excess of CH_2N_2 in Et_2O and evaporated to dryness. Residue was washed with $CHCl_3$ (5 × 1 ml) and the $CHCl_3$ phase was evaporated to dryness. Residue was crystallised from Et_2O–hexane at −20°C giving trimethyl citrate (14 mg), mp 76–78°C (lit. [7] mp 78.5–79°C). The total amount of trimethyl citrate was found by GLC to be 17.5 mg. The residue insoluble in $CHCl_3$ above was dissolved in H_2O and the soln washed with $CHCl_3$–MeOH (1:1). The aq phase was evaporated to dryness giving *p*-cresyl-β-D-glucopyranoside (68 mg), mp 181–182.5°C; $[\alpha]_D^{22}$ − 66° (*c* 0.27, H_2O).

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NEOCAPILLEN, A NEW ACETYLENIC HYDROCARBON FROM *ARTEMISIA CAPILLARIS*

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Key Word Index—*Artemisia capillaris*; Compositae; acetylenic hydrocarbon; neocapillen.

Abstract—During an investigation of *Artemisia capillaris*, a new acetylenic hydrocarbon, neocapillen, was isolated as a minor component and its structure determined.

The structures of the new acetylenic compounds, 1-(2'-methoxyphenyl)-2,4-hexadiyne (*o*-methoxy capillen), capillanol and norcapillen, in the essential oil of the stalks and leaves of *Artemisia capillaris* was described previously [1-3]. As a continuation of our study on the components of *A. capillaris* extracts, which have been recognized to make an important contribution to the characteristic odour, we wish to report the identification of a new polyacetylenic hydrocarbon neocapillen (**1**), which seemed to be derived from capillen (**2**) [4].

Fresh roots of *A. capillaris* were chopped finely and extracted with ether. The extract was chromatographed on alumina and divided into 3 fractions from which compound **1**, which had a Shiitake-like odour, was isolated by PLC.

By elementary analysis, the molecular formula of **1** was determined to be $C_{12}H_{10}$ (Found: C, 93.44; H, 6.56; Calcd.: 94.46; H, 6.54%). The spectral data of **1** are given in the Experimental. The IR showed absorptions at 2210, 2200 and 2120 cm^{-1}(–C≡C–), at 1595 and 1490 cm^{-1} (aromatic), and at 755 and 690 cm^{-1} (aromatic H). These data indicated that the compound was an aromatic mono-substituted hydrocarbon with a C_6H_5 unit. The IR absorptions at 1210 and 1120 cm^{-1} and the intense UV absorption at 222 nm in *n*-hexane indicated the presence of a 1-phenyl-1,3-dyne function [5]. The NMR spectrum showed no olefinic proton, a signal at δ 2.16(2H) was the two protons of a methylene attached to a conjugated diacetylenic bond. The five protons in the benzene ring appeared as a broad singlet from δ 7.05 to 7.55. Consequently, the splitting pattern of the signals in the NMR spectrum were consistent with structure (**1**) for neocapillen. It had a UV spectrum almost super-imposable with that of norcapillen [3].

Besides the molecular ion peak at *m/e* 154 the other significant MS peaks were at *m/e* 153(M^+-H, 82%), 152(M^+-H_2, 47%), 139(Ph–C≡C–C≡C–CH_2^+, 36%), 113 (Ph–C≡C–C^+, 7%).

For the confirmation of the identity, compound **1** was prepared from capillen. Good agreement of the IR, NMR and MS spectra was observed between neocapillen (**1**) and the synthetic material. **1** may be an artefact produced from **2** by UV irradiation, although no acetylenic substance has been detected in the upper parts of the plants. **1** was catalytically hydrogenated over PtO_2 in ethanol to give octahydroneocapillen, which was found to be identical with *n*-hexylbenzene in all respects (IR, NMR, MS spectrum). Thus, the structure of neocapillen was confirmed to be 1-phenyl-1,3-hexadiyne. The synthesis of this phenylacetylene had been reported [6]. Many phenyl diacetylene (Ph–C≡C–C≡C–R) derivatives which have C_7 or C_{11}-side chains have been detected in the genus *Bidens*, *Coreopsis* and *Dahlia*.

Ph–C≡C–C≡C–CH_2Me
(**1**)

Ph–CH_2–C≡C–C≡C–Me
(**2**)

The first isolation of neocapillen from a natural source is significant from biogenetic considerations as all the phytoacetylenes so far isolated, have a phenyl diacetylene skeleton or a modification thereof.

EXPERIMENTAL

UV spectra were measured in EtOH. NMR spectra were determined at 60 MHz, in CCl_4 and with TMS as internal standard.

Plant material and oil removal. Fresh roots (5 kg) of *A. capillaris*, collected in October at the suburbs of Osaka prefecture, were chopped finely and extracted with Et_2O for 5 weeks at room temp. Neocapillen was also obtained after only several hr extraction.

Isolation of neocapillen (**1**). The extract (15.8 g) was chromatographed on deactivated alumina with *n*-hexane, C_6H_6 and Et_2O, and divided into 3 fractions. Elution with C_6H_6 gave neocapillen (**1**) which was then isolated by PLC (R_f 0.60) developed with *n*-hexane–EtOAc (6:1). MS *m/e* (rel. int.): 154(100%) M^+, 153(82), 45(63), 152(47), 139(36), 73(29); 89(24), 88(22), 43(20), 151(18). IR $\nu_{max}^{cm^{-1}}$: 3025, 3005, 2960, 2900, 2855, 2825, 2210, 2200, 2120, 1943, 1880, 1595, 1570, 1490, 1450, 1440, 1425, 1375, 1330, 1290, 1170, 1150, 1065, 1050, 1020, 950, 785, 755, 690. UV λ_{EtOH}^{max} nm: (log ϵ) 211 nm (3.42), 222(3.55), 244(2.63), 257(3.13), 272(3.32), 289(3.20). NMR: δ 1.00(3H, *t*, *J* = 6.2 Hz), 2.16(2H, *q*, *J* = 6.2 Hz), 7.05 ~ 7.55(5H, *m*).

Catalytic hydrogenation of **1**. Catalytic hydrogenation of **1** (50 mg) in EtOH (5 ml) over PtO_2 (1.4 mg) was carried out at room temp for 3 hr. The product was purified by GLC (Carbowax-20 M 5%, 80 ~ 100 mesh, 4 mm × 3 m, 1.5 Kg/cm^2), to give a colourless oil, NMR: δ 0.88(3H, *t*, –CH_2–C$\underline{H}_3$), 1.26(8H, *m*, –($C\underline{H}_2$)$_4$–), 2.68(2H, *t*, ϕ–C$\underline{H}_2$–), 7.23(5H, *m*, ϕ–). (Found: C, 88.80; H, 11.20; Calcd for $C_{12}H_{18}$: C, 88.81; H, 11.19.)

Isolation of capillen (**2**) The essential oil from stalk and leaves of a *A. capillaris* was chromatographed on activated alumina (60 g, 300 mesh) with *n*-hexane, C_6H_6, Et_2O, EtOAc and EtOH, and divided into 5 fractions. Subsequent elution with C_6H_6 gave capillen (**2**) which was then isolated by prep GLC, and identified (UV, IR, NMR) by comparison with an authentic specimen [4,7].

Catalytic hydrogenation of **2**. Catalytic hydrogenation of **2** (55 mg) in EtOH (5 ml) over PtO_2 (1.5 mg) was carried out at room temp for 3.5 hr. The product was purified by prep GLC. NMR: δ 0.88 (3H, *t*, –CH_2–C$\underline{H}_3$), 1.26(8H, *m*, –($C\underline{H}_2$)$_4$–), 2.68(2H, *t*, ϕ–CH_2–), 7.23(5H, *m*, ϕ–). MS *m/e*: 162(M^+, 26%).

Irradiation of capillen (**2**). **2** (50 mg) dissolved in a mixture of 70 ml MeOH and a trace of KOH were irradiated for about 24 hr in a Pyrex tube with light of wavelength 3500 Å. This soln was acidified and extracted with Et_2O; the extract was washed, dried and evaporated to leave a viscous reddish oil. After separation by prep GLC 10 mg of neocapillen (**1**) were obtained as a pure compound.

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