[Chem. Pharm. Bull. 19(3) 638—640 (1971)]

UDC 547.597.02 : 581.192

Components of the Root of *Acorus calamus* L.

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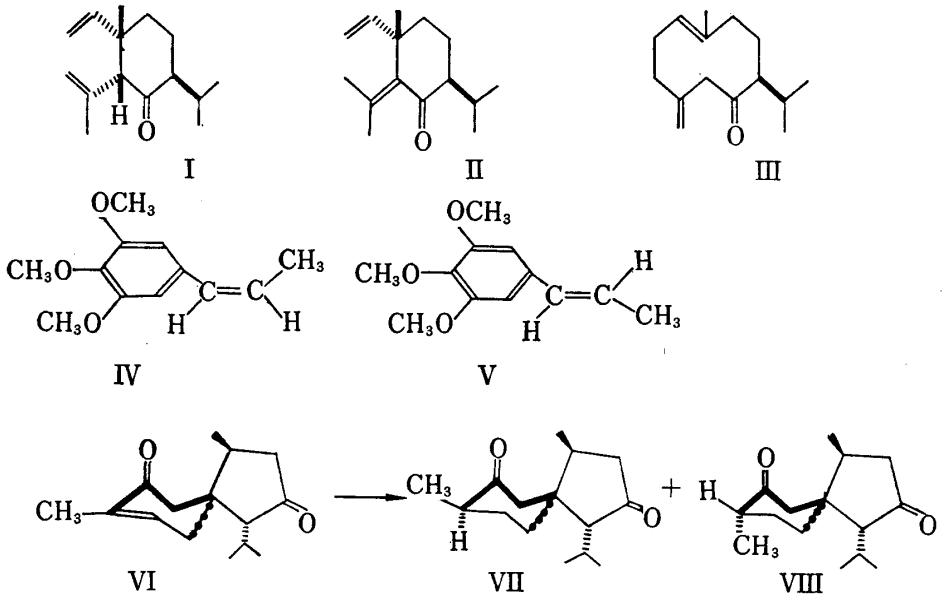
(Received September 10, 1970)

A number of investigations[2] had been done on the components of sweet flag oil. Recently, some sesquiterpenes[3,4] have been isolated from the root of *Acorus calamus* L. (Shyobu in Japanese) growing in Japan and their structures been elucidated.



For the purpose of obtaining some materials for the study of Cope rearrangement, components of the root of this plant were further investigated. The ether extract was separated by alumina chromatography and preparative thin-layer chromatography (TLC) on silica gel to give a new sesquiterpene, named acoronene, in addition to epishyobunone[3] (I), isoshyobunone[3] (II), (III),[4] asarone[5-7] (IV), and β-asarone[5,7] (V). We wish to report here the structure of acoronene.

Acoronene (VI), $C_{15}H_{22}O_2$, mp 69°, $[\alpha]_D$ +66.8° showed infrared (IR) peaks at 1740 (five-membered ring ketone) and 1680 cm^{-1} (α,β-unsaturated ketone) and an ultraviolet (UV) absorption band at 238 mμ (ε 7650) (enone). In the nuclear magnetic resonance (NMR)

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spectrum, it showed signals at δ 0.92 (d, J=6.7 Hz, CH_3), 1.77 (vinylic CH_3), and 6.70 ppm (1H, vinylic). These data agree with structure (VI) for acoronene.

In order to confirm this structure, acoronene was hydrogenated with 5% palladium-charcoal in methanol to give a mixture of compounds (VII) and (VIII), which was separated by preparative TLC on silica gel.

Compound (VII), $C_{15}H_{24}O_2$, mp 99—99.5°, $[\alpha]_D$ −80.3° showed IR peaks at 1741 and 1718 cm^{-1}, and these physical data and IR spectrum were identical with those of isoacorone.[8] Compound (VIII), $C_{15}H_{24}O_2$, mp 93—95°, $[\alpha]_D$ +106.2° was also identical with acorone[8] by comparisons of mp, IR, and $[\alpha]_D$ value.

The stereostructure of acorone was elucidated by X-ray analysis[9] of its *p*-bromophenylsulphonyl hydrazone as shown in the formula (VIII). Therefore, acoronene should be represented by the formula (VI).

Experimental

NMR spectra were taken for solutions in deuteriochloroform with a Varian A 60 spectrometer and UV spectra for solutions in 95% ethanol. mp were measured with Kofler hot-stage apparatus. Silica gel G (Merck) was used for TLC.

Isolation of Acoronene (VI)——The dried and sliced root (2 kg) of the plant was extracted with ether (3×31) at room temperature. The ether extract was washed with 5% sulphuric acid, 5% sodium carbonate, and water, dried (Na_2SO_4), and evaporated *in vacuo* to leave an oil (120 g). This neutral extract (5 g) was dissolved in light petroleum (250 ml) and chromatographed on neutral alumina (150 g; "Woelm" Activity Grade III) as shown in the TableI.

Table I. Chromatogram of the Neutral Ether-extract (5 g)

Fraction No.	Solvent	Ti yield (mg)
1— 4	light petroleum	1380
5— 7	light petroleum–ether (9:1)	880
8—11	light petroleum–ether (9:1)	420
12—17	light petroleum–ether (8:2)	410
18—21	light petroleum–ether (7:3)	170
22—23	light petroleum–ether (1:1)	168
24	methanol	70

Fraction nos. 1—4 (1380 mg) were dissolved in light petroleum (100 ml) and rechromatographed on alumina (30 g), and then separated by preparative TLC (benzene:ether=95:5) into epishyobunone (I, 30 mg), a colourless oil, bp 58—63°/0.5 mm, *Rf* 0.89, M^+ 220, $\nu_{max}^{CCl_4}$ 1712 and 1643 cm^{-1} (Found: C, 81.63; H, 11.07. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%), NMR of which was completely identical with the data of epishyobunone,[3] and a colourless oil (III, 40 mg), bp 80—83°/3 mm, *Rf* 0.75, $[\alpha]_D^{22}$ −35.8° (±2.1°) (c=0.360 in chloroform), $\nu_{max}^{CCl_4}$ 3080, 1710, 1645, and 899 cm^{-1} (Found: C, 82.11; H, 11.06. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%), NMR of which was identical with the data of III.[4]

Fraction nos. 5—7 were rechromatographed on alumina and then separated by preparative TLC (benzene:ethylacetate=95:5) into isoshyobunone (II), a colourless oil, bp 64—67°/0.5 mm, *Rf* 0.70, M^+ 220, $\nu_{max}^{CCl_4}$ 1679 cm^{-1} (Found: C, 81.50; H, 10.75. $C_{15}H_{24}O$ requires C, 81.76; H, 11.07%), NMR of which was identical with the data of isoshyobunone,[3] and an asarone mixture, *Rf* 0.67, which was separated by preparative GLC (gas liquid chromatography) (a 5% SE-30 column, 3.3 m in length with a 10 mm i.d., 160°, He 100 ml/min) into asarone[5] (IV), a colourless oil, retention time 28.5 min, $\nu_{max}^{CCl_4}$ 1401 and 860 cm^{-1} (Found: C, 69.36; H, 7.81. $C_{12}H_{16}O_3$ requires C, 69.21; H, 7.74%) anf *β*-asarone[5] (V), a colourless oil, retention time 22.5 min, $\nu_{max}^{CCl_4}$ 1410, 1395, 865, and 855 cm^{-1} (Found: C, 69.11; H, 7.74%).

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Fraction 8—11 (420 mg) was rechromatographed on alumina and then separated preparative TLC (benzene:ether=95:5) to give acoronene (VI, 75 mg), colourless prisms, mp 69° (from *n*-hexane), *Rf* 0.31, M+ 234, $[\alpha]_D^{23.5}$ +66.8° (±1.0°) (*c*=1.039 in dioxan), λ_{max} 238 mμ (ε 7650), $\nu_{max}^{CCl_4}$ 1740, 1680, and 928 cm^{-1}, NMR δ 0.92 and 1.00 (isopropyl), 1.08 (CH_3), 1.77 (CH_3), and 6.70 ppm (1H). Found: C, 77.07; H, 9.45. $C_{15}H_{22}O_2$ requires C, 76.88; H, 9.46%.

Hydrogenation of Acoronene (VI)——A solution of VI (30 mg) in methanol (3 ml) was hydrogenated with 5% palladium-charocoal (30 mg) at room temperature. The product showed two spots, *Rf* 0.49 and 0.31 on TLC (benzene:ether=95:5) and then separated by preparative TLC into isoacorone (VII, 20 mg), colourless needles, mp 99—99.5° (from ether), *Rf* 0.49, M+ 236, $[\alpha]_D^{22}$ −80.3° (±5.3°) (*c*=0.228 in ethanol), $\nu_{max}^{CHCl_3}$ 1741 and 1718 cm^{-1} (Found: C, 76.37; H, 10.17. $C_{15}H_{24}O_2$ requires C, 76.22; H, 10.24%), which was identical with the data of isoacorone[8] [IR ($CHCl_3$ and CS_2), mp, and $[\alpha]_D$] and acorone (VIII, 10 mg), colourless needles, mp 93—95° (from ether), *Rf* 0.31, M+ 236, $[\alpha]_D^{22}$ +106.2° (±6.1°) (*c*=0.241 in ethanol), $\nu_{max}^{CHCl_3}$ 1741 and 1718 cm^{-1} (Found: C, 75.71; H, 10.76%), which was identical with the data of acorone[8] [IR ($CHCl_3$ and CS_2), mp, and $[\alpha]_D$].

[Chem. Pharm. Bull. 19(3) 640—642 (1971)]

UDC 547.587.51.02.05 : 581.192

Coumarins from the Roots of *Angelica laxiflora* Diels

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(Received September 26, 1970)

In a previous communication,[2] it was reported that the ether extract of the Chinese crude drug "Chuan Duhuo (川独活)," the source of which had been unknown but to be dried roots of a species of *Angelica genus*, upon vacuum distillation afforded 6-formyl-7-methoxy-coumarin, named angelical which was first isolated from the ether extract of the roots of *Angelica pubescens* Max. upon vacuum distillation[3] and was later proved to be an artefact from angelol,[4] and a crystalline compound, mp 115—116°, analytical data of which was in accord with the molecular formula $C_{15}H_{16}O_4$.

As a part of our continuing study of the coumarins from the *Umbelliferous* plants, we have reinvestigated the constituents of "Chuan Duhuo" recently obtained from the Xiang-gang (香港) market, which is assigned to the dried roots of *Angelica laxiflora* Diels. according to the ref. 5).

The ether extract of the crude drug upon chromatography over silica gel followed by elution with a mixture of *n*-hexane and ethyl acetate afforded bergapten, umbelliferone and angelol, identified by the mixed melting point examination with the authentic samples, as well as three compounds, $C_{14}H_{14}O_4$ (I), mp 162—163°, $C_{16}H_{16}O_5$ (II), mp 130—131°, and $C_{19}H_{20}O_5$ (III), mp 116—117°, which were identified as columbianetin,[6] columbianetin acetate and columbianadin,[6] respectively, on the basis of the evidences described in the sequel.

I was suggested to be identical with columbianetin from the analytical data, the melting point and the optical rotation, and this was confirmed from the nuclear magnetic resonance

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