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(−)-(9*Z*)-1,9-Heptadecadiene-4,6-diyn-3-ol as a Principal Component of the Resinous Sap of Evodiopanax innovans Nakai, Japanese Name, Takanotsume, and Its Role in an Ancient Golden Varnish of Japan[1)]

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(−)-(9*Z*)-1,9-Heptadecadiene-4,6-diyn-3-ol was for the first time isolated in high yield (29%) from the resinous sap of Evodiopanax innovans Nakai, Araliaceae. This compound has been associated with the main polymerizable component of an ancient golden varnish. It has also been associated with a phytoalexin and a defense material which produces a water-insoluble coating film by photopolymerization under sunlight for a Takanotsume tree upon being wounded.

(−)-(9*Z*)-1,9-Heptadecadiene-4,6-diyn-3-ol, also called panaxynol,[2)] falcarinol,[3)] and carrotatoxin,[4)] was first isolated in high yield as the main component of the resinous sap of the Takanotsume tree; it was previously used as one of the GONZETSU paints in Japan. GONZETSU was a golden-colored, anticorrosive paint varnish (photopolymerizable by sunlight) used for armor suits and helmets in ancient Japan, Korea, and China.[5)] GONZETSU paint used in ancient Japan had been named as KOSHIABURA and was thought to be the resinous sap of the Koshiabura tree (Acanthopanax sciadophylloides French et. Sav., Araliaceae),[6)] though its correct origin remained unproven until recently.[7)]

Terada[8)] studied the historical documents concerning GONZETSU, as well as the floras of the Koshiabura tree and similar trees such as Kakuremino and Takanotsume trees, Araliaceae in Japan. He also investigated the chemical constituents of their resinous saps, arriving at the conclusion that in Korea and China during the T′ ang dynasty the GONZETSU was called ŌSHITSU (yellow varnish), the resinous saps of trees of the Dendropanax genus (Araliaceae family; these plants belong to one and the same genus of Japanese Kakuremino tree, namely, Dendropanax morbifera Leb., in Korea, and Dendropanax chevalieri (Viquier) Merr., in Chechiang-Sheny of China). He also concluded that in Japan the resinous saps of trees of Koshiabura, Takanotsume, and Kakuremino (Dendropanax trifidus Makino) were used for the same purpose.[9)] The saps of the former two were the indigenous Japanese golden varnish GONZETSU; their fast-drying abilities were so valuable that they were exported to T′ ang and Po-hai in ancient times.[9)] All of them were called either GONZETSU or KOSHIABURA in Japan, and were photosensitive paints which could harden under sunlight irradiation.[9)]

We have already reported on the chemical constituents of the resinous saps of Koshiabura and Japanese Kakuremino,[10,11)] and recently found that they contained polyacetylenic compounds.[12)] The present report deals with the detection of a polyacetylenic compound((−)-(9*Z*)-1,9-heptadecadiene-4,6-diyn-3-ol) as the main component of Takanotsume resinous sap as well as its sunlight polymerization and biological roles.

Results and Discussion

The ethanolic extract of Takanotsume sap (**1**) was a red brown oil, and showed conjugated polyacetylenic absorption bands in IR and UV which implied an ene–diyne conjugated system.[13)] Since this sample accompanied many mono- and sesquiterpenes and polymers and was very labile, catalytic hydrogenation at ordinary temperature and pressure was carried out and gave white crystals: $C_{17}H_{36}O$, mp 51.5—52 °C in 27% yield. ^{13}C NMR and other analytical evidence showed that this was 3-heptadecanol (**2**).

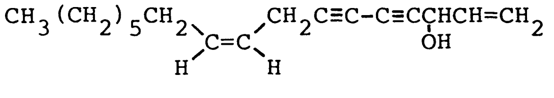
Repeated TLC separations of the crude sample (**1**) of polyacetylenes afforded an analytical sample, $C_{17}H_{24}O$ (**3**) in 29% yield, which showed $[\alpha]_D^{18}$ −36.93°; the IR spectrum was identical with that of (−)-(9*Z*)-1,9-heptadecadiene-4,6-diyn-3-ol, panaxynol, isolated and identified already by Takahashi et al.[2a)] from the Ginseng root (Panax ginseng C. A. Meyer) in 0.1% yield. This was also identical with the carrotatoxin isolated in a trace amount (between 10 and 20 ppm) as a natural toxicant from vegetable carrot (Daucus carota L.) by Crosby and Aharonson,[4)] and with falcarinol from Falcaria vulgaris Bernh and from many other Umbelliferae by Bohlmann et al.[3)] All of them were shown to be the same compound by Bently et al.[14)]

The MnO_2 oxidation of **3** resulted in the formation of (9*Z*)-1,9-heptadecadiene-4,6-diyn-3-one (**4**), also proving the existence of **3** in Takanotsume sap.

Compound **3** polymerizes in sunlight to produce a golden, transparent, hard film that is insoluble in solvents. In general, a conjugated polyacetylenic compound quickly polymerizes under daylight[15)] or UV-light irradiation,[16)] and the following polymer structure, like **5** in Fig. 1 for example, may be typical in the case of the conjugated diacetylene (**3**).[16)] Upon polymerization, the carbon–carbon double bonds in the R and R′ groups (Fig. 1) may be co-operative during polymerization. The IR- and UV-absorption spectra of the dried film **5** are shown in Figs. 2 and 3, respectively, along with those of **3**.

The IR-absorption bands of the monomer **3** at 2255 (C≡C–C≡C, strong), 983 and 929 (vinyl), and 692 cm^{-1} (C=C, cis) were absent in the polymer film (**5**). Moreover, new characteristic bands of the polymer (**5**) appeared at 2195, 2155, and 2120 (C≡C–C=C, conjugated, all weak), and at 979 and 955 cm^{-1} (C=C, conjugated). Tieke et al. ascribed these phenomena to the C≡C-streching modes of the polymer backbone with various C–C-skeleton motions, judged from a large number of small peaks around them.[18] In addition, the structure of the polymer was supported by the finding of Baughman et al. that the polymer backbone was best represented by (=C–C≡C–C=)$_n$ from its Raman spectra.[19] These facts show that the polymer backbone is built up by a structure like **5** in Fig. 1.

The UV of polymer **5** in Fig. 3 shows a bathochromic shift and the polymer color is, therefore, a golden-yellow. Usually, to make Langmuir–Blodgett multilayers a number of conjugated diacetylenes are employed in solid state polymerization by irradiation of the UV light from a high-pressure mercury lamp; the



$C_{17}H_{24}O$ (**3**)

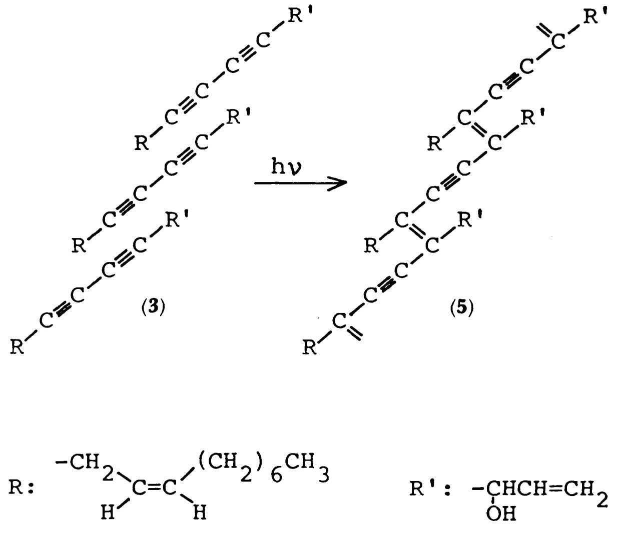


Fig. 1. Photopolymerization of **3**.

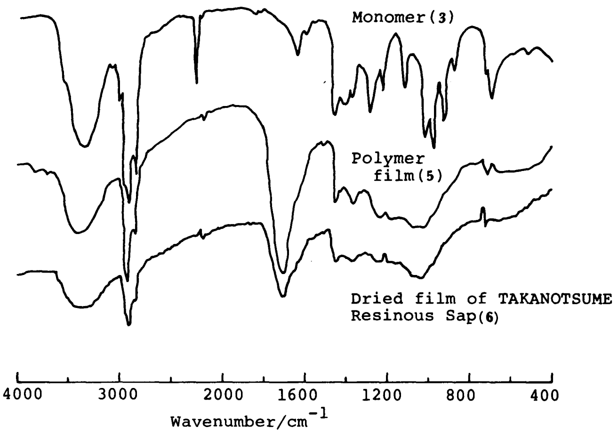


Fig. 2. IR of monomer **3**, polymer **5**, and dried film of TAKANOTSUME resinous sap.

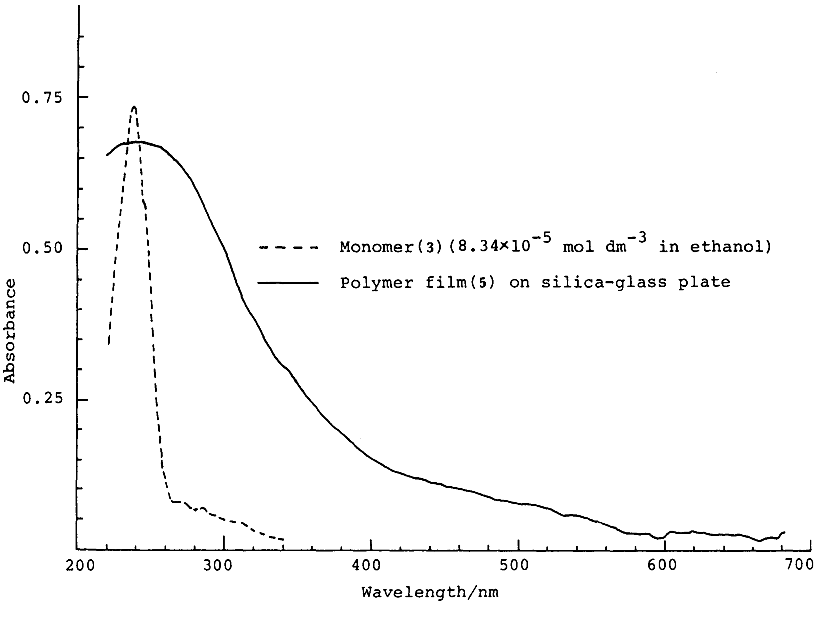


Fig. 3. UV of monomer **3** and polymer **5**.

reactions come to completion within a few minutes. These polymerizations proceed topochemically without any destruction of the layer structures, and appear as deep purple; this color changes irreversibly to red upon treatment with ethanol or chloroform.[16] Because the net-worked insoluble polymer **5**, which we obtained in this study, is not such a high-molecular-weight one and does not have such a stereoregularity, it therefore shows a golden-yellow color owing to the short-distance conjugation of carbon–carbon double and triple bonds in the polymer backbone. Krieger said that a polymer having a highly planar backbone is blue, that a slightly planar one is red, and that a highly nonplanar one is yellow.[20]

We also show the IR of a dried fim of Takanotsume sap in Fig. 2-**6**. This is almost the same with that of the polymer **5**.

The above-mentioned facts prove that this sap would be one of the old GONZETSU paint-compounds which made the old armors and helmets golden-colored, waterproof and anticorrosive.

Yoshioka et al.[21] have reported that the hexane extract of Takanotsume stems showed no conjugated polyacetylenic compound on its UV-spectral detection. Thus, our finding that compound **3** occurs only upon cutting the bark to obtain sap would suggest that this is a phytoalexin which can be used as an antiseptic. Dewit and Kodde have reported this compound **3**, falcarinol, as a phytoalexin, which was found in tomato (Lycopersicon esculentum) after incubation with Cladosporium fulvum.[22] Harding and Heale have found falcarinol to be one of the inhibitory compounds in the induced resistance response of carrot root slices; the compound was active against Botrysis cinerea.[23] We also suppose that the compound **3** that we obtained here acts effectively as defensive-type substance through a phytoalexin and also by forming a coating film over a raw wound. These phenomena suggest that compound **3** would play a similar role to Japanese lacquer urushiol found in the sap of Rhus verniciflua Stokes.

Otsuka et al. have found a strong inhibitory activity of the chloroform extract of roots of Panax ginseng C. A. Meyer against the formation of granulation tissue and proved that compound **3** and linoleic acid were the major active components.[24]

In Japan, especially in Northeast districts (Tohoku), some people have a well-established custom of eating the young leaves of Takanotsume. They also feed domestic animals the leaves since the tree is of little importance these days. Yasue et al.[25] have reported an accident in which some goats were poisened after eating this food. We suppose that since many polyacetylenic compounds are well known to be poisonous to fish,[26] and that compound **3** has been found as a natural toxicant by Crosby and Aharonson,[4] such a poisoning might suggest an accumulation of compound **3** as well as closely related polyacetylenic compounds in their food leaves.

We also conclude again that the occurrence of a great quantity of compound **3** in a wounded Takanotsume tree is for phytoalexin and serves as a barrier against the raw wound through polymerization; it then makes its own cure.

Experimental

Infrared and ultraviolet absorption spectra were recorded on Hitachi 260-30 infrared and Hitachi 139 UV spectrophotometers, respectively. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM-FX 60 spectrometer operated at 60 and 15.04 MHz, respectively. Mass spectra were determined on a JEOL DX-300 spectrometer. Mp's(corrected) were determined on a Yanagimoto micromelting point apparatus. TLC separations were performed by silica gel(Merck, 60 PF).

Ethanolic Extract of Takanotsume sap. Takanotsume sap was dissolved in ethanol, filtered and concentrated under diminished pressure to give an orange-yellow oil (**1**). IR (neat) 3380 (broad, OH), 2250 (sharp, $-C{\equiv}C-$), 2230 (weak, $-C{\equiv}C-$), 1640 ($-C{=}C-$), and 698 cm^{-1} (cis $-CH{=}CH-$). The benzene extract of **1** showed the UV$_{max}$ (methanol) at 228, 237, 254, 269, and 285 nm. This orange-yellow oil (**1**) spread on a glass plate was dried under sunlight irradiation for half an hour,[1] resulting in the formation of a golden-colored, transparent, hard film.

Catalytic Hydrogenation of Ethanolic Extract of Takanotsume sap. Upon hydrogenation using a platinum black catalyst in ethanol under ambient temperature and atmospheric pressure, 1.740 g of the ethanolic extract (**1**) absorbed 551.6 ml of hydrogen and yielded 27% of white crystals, mp 51.5—52 °C, after purifications by silica-gel column chromatography and recrystallization from ethanol. The ^{13}C NMR data showed that this compound was an open chain alcohol, 3-heptadecanol (lit , mp 54—54.5 °C,[2a] 44—46 °C,[4]) and the IR spectral data well agreed with those reported.[4] IR (KBr) 3320, 3220 (each OH), 1473 (CH_2), 1380, 1348 (each CH_3), 1139 (OH), 948, and 723 cm^{-1}; MS *m/z* 256 (M^+), 238 ($M^+ - H_2O$), 227 ($M^+ - CH_3CH_2$), 197 ($C_{14}H_{29}$), 59 ($C_2H_5CH(OH)$); ^{13}C NMR ($CDCl_3$) δ=9.9 (q, C-1), 14.2 (q, C-17), 22.7 (t, C-16), 25.8 (t, C-5), 29.4 (t, C-6, C-14), 29.7 (t, C-7—C-13), 30.2 (t, C-2), 32.0 (t, C-15), 37.0 (t, C-4), and 73.4 (d, C-3). Found: C, 79.57; H, 14.34%. Calcd for $C_{17}H_{36}O$: C, 79.61; H, 14.15%.

Isolation of 3. An ethanolic extract of a fresh Takanotsume sap was repeatedly chromatographed by TLC and gave 29% of a light-yellow oil (**3**) (R_f=0.33, $CHCl_3$), $[\alpha]_D^{18}$ −36.93° (*c* 0.77, $CHCl_3$) (lit, −25.2°).[2a] UV(95%C_2H_5OH) λ_{max} 238 (ε=8700); IR (neat) 3330 (OH), 3090, 3020 ($C{=}C{-}H$), 2255 ($C{\equiv}C$), 1638 ($C{=}C$), 1118 (OH), 1015, 983, 930 (vinyl), and 698 cm^{-1} (cis $-CH{=}CH-$);[2d] MS *m/z* 244 (M^+, 6%) and 159 ($M^+ -[-(CH_2)_5CH_3]$); ^{1}H NMR ($CDCl_3$) δ=0.81 (3H, m, CH_3), 1.28 (10H, m, $CH_2{\times}5$), 2.0 (2H, m, $={CH}{-}C\underline{H}_2-$), 3.12 (2H, d, *J*=6 Hz, $\equiv CC\underline{H}_2{-}CH=$), 4.88 (1H, d, *J*=4.8 Hz, $C\underline{H}OH$), 5.4 (2H, m, vinyl $CH_2=$), 5.85 (1H, ddd, *J*=4.8, 9.4, 17 Hz, vinyl), and 5.45 (2H, m, $-CH{=}CH-$). Found: C, 83.08; H, 9.62%. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.80%.

(9Z)-1,9-Heptadecadiene-4,6-diyn-3-one (4). By the procedure of Takahashi and Yoshikura,[2b] MnO_2 oxidation of 80 mg of **3** in hexane afforded 41 mg of a pure sample of **4**

after the usual work-up, a yellow oil. The IR was identical with those of Takahashi and Yoshikura[2b] and Bohlmann et al.[27] IR (neat) 3010 (C=CH), 2240 (C≡C), 1642 (C=O), 1614(C=C), 1462, 1402, 1311, 1272, 1163, 1078, 982, and 967 (vinyl), 905, 795, 703, and 686 cm^{-1} (cis C=C). There was no appearance of an OH band in the 3500—3300 cm^{-1} region.

Photopolymerization of 3. A sample of **3** was spread to a thickness of 20 μm on a glass plate using an applicator, and exposed directly to the sun for 1 h. Polymerization was almost completed within this time and the color changed to golden yellow (Fig. 1). The dried film showed 33 in hardness according to a Swoad-Rocker Hardness test (the hardness of the standard glass plate is provided as 100).[17] The IR and UV spectra are shown in Figs. 2 and 3, respectively.

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