IR-120 (H^+) (100 ml) and 2 M NH_4OH (1 l.). NH_3 was removed by concentration. 11 M HCl (1/10 vol.) was added to the resulting soln and oxides of nitrogen, generated from $NaNO_2$ and HCl, were bubbled in a stream of N_2 into the mixture until the ninhydrin-test was negative. The mixture was then extracted ×4 with Et_2O. The Et_2O layers were combined and evaporated to a syrup. 11M HCl (30 ml) was added and the mixture boiled under reflux for 45 min. HCl was reduced by concn. For the final purification, a column of Dowex 50W × 8 (200–400 mesh, H^+, 2.5 × 85 cm) and 1.5M HCl were used. The relevant fractions were combined and concnd twice with addition of small amount of H_2O. The crystals of hydrochloride separated were collected, washed with EtOH and dried (90 mg). They were recrystallized ×3 from H_2O and Me_2CO. Mp 216–20° (decomp), (lit. [3] 210–5° (decomp). $[\alpha]_D^{24} = -9.7°$ (c = 0.93, H_2O), (lit. [3] $[\alpha]_D^{20} = -10.9°$ (c = 0.92, H_2O). $C_6H_{11}NO_3$.HCl (Found: C 39.65; H 6.91; N 7.55; Cl 19.59. Calcd.: 39.68; H 6.66; N 7.71; Cl 19.52). *cis*-5-Hydroxy-L-pipecolic acid was eluted just after its *trans*-isomer from the system of Dowex 50 and 0.2M citrate buffer, pH 3.3. The fractions (92–200) were combined, desalted and treated with nitrous oxides as before. The nitrosoamino acids were extracted with Et_2O and reconverted to the free imino acids by refluxing in HCl. As a large amount of proline was present in the soln, it was removed using a Dowex 50W-column (H^+) and 1.5M HCl. The fractions containing only *cis*-5-hydroxypipecolic acid were combined (280 ml) and concnd. After the bulk of HCl had been removed, crystals of *cis*-5-hydroxy-L-pipecolic acid hydrochloride separated (470 mg). Recrystallization was repeated ×3 from aq. EtOH and Et_2O. mp 183–5° (decomp). $[\alpha]_D^{24} = -18.5°$ (c = 1.0, H_2O). Hydrobromide, mp 200–1°, (lit. [3] 205–7°). Free amino acid, mp 229–31° (decomp), (lit. [3] 255–8° (decomp)). $[\alpha]_D^{24}$ −32° (c = 0.8, H_2O), (lit. [3] $[\alpha]_D^{20}$ −31.1° ± 0.2 (c = 0.8, H_2O)). $C_6H_{11}NO_3$.HCl (Found: C 38.83; H 6.53; N 7.90; Cl 19.93. Calcd: C 39.68; H 6.66; N 7.71; Cl 19.52).

Isolation of cis-*5-hydroxy-L-pipecolic acid from seeds of* Lathyrus japonicus. Seeds (360 g) were powdered in a mill, defatted with Et_2O (3 l.) and dried. They were then extracted ×4 with 80% EtOH. The filtered extract (10.6 l.) was treated with Amberlite IR-120 (H^+) (300 ml) and the amino acids were eluted with 2M NH_4OH (3 l.). The NH_4OH eluate was concd to a small vol. and fractionated on a column of Dowex 1 × 4 (OAc^-, (4 × 90 cm)) and 0.2M HOAc. The fractions containing basic and neutral amino acids were combined, concnd to a small vol. and applied to a column of Dowex 50W (Na^+, 3.1 × 58 cm). Fractionation was achieved with 0.2M citrate buffer, pH 5. Neutral amino acids, which passed rapidly through the column, were, after desalting, fractionated further with Dowex 50W (Na^+, (3.1 × 58 cm)) and 0.2M citrate buffer, pH 3.3. During this procedure pure fractions of *cis*-5-hydroxy-L-pipecolic acid were obtained; they were desalted as before. The NH_4OH eluate was concnd to a small vol., taken up in aq. EtOH and Me_2CO was added. The separated free amino acid was recrystallized ×3 from aq. EtOH (192 mg). mp 230–5° (decomp). $C_6H_{11}NO_3$ (Found: C 49.00; H 7.28; N 9.59. Calcd: C 49.65; H 7.64; N 9.65). Hydrochloride, mp 184–7° (decomp), $[\alpha]_D^{24}$ −18.5° (c = 1.0, H_2O).

PC Data. Values of R_{Ala} of the isolated *trans*- and *cis*-form with solvent (c) were 1.31 and 1.0, respectively (descending, 75 hr) (lit. [7], 1.31 and 1.0) and with solvent (b) 1.22 and 1.38, respectively.

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13-HYDROXYHENTRIACONTAN-16-ONE FROM *NEOLITSEA SERICEA*

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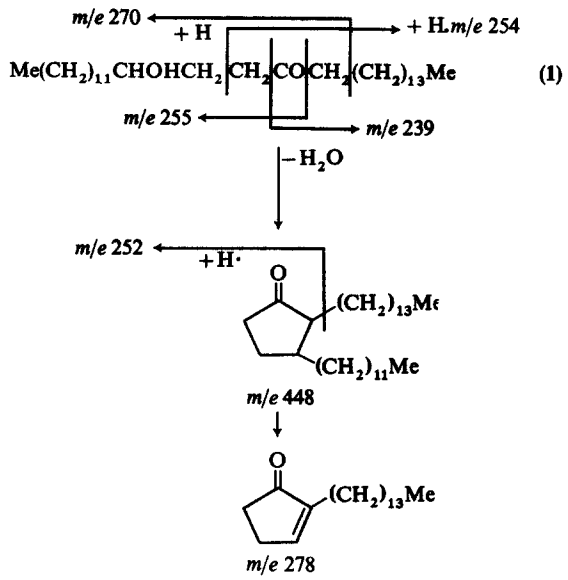
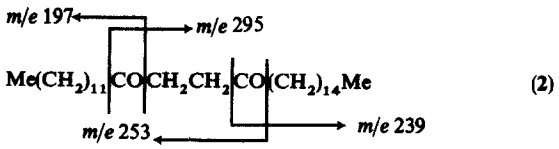
Key Word Index—*Neolitsea sericea*; Lauraceae; γ-hydroxyketone; 13-hydroxyhentriacontan-16-one.

The essential oil of the leaves of *Neolitsea sericea* Koidz. (*Neolitsea sieboldii* Nakai, *Litsea glauca* Sieb.) from southern parts of Japan and China had been investigated to isolate sericealactone etc. [1]. In the course of our studies on the lignoids of the Lauraceae we examined a Me_2CO extract of the fresh leaves of this plant and isolated 13-hydroxyhentriacontan-16-one which has not been previously found in nature. No lignan could be isolated. In this paper we wish to report its isolation and structural determination.

The Me_2CO extract was concentrated to give a deposit, a mixture of glycosides of flavones, which is under investigation. The filtrate was then extracted with hexane. After concentration the hexane extract was steam-distilled to remove volatile components. The residue was dissolved in hexane and chromatographed on a neutral Al_2O_3 column with hexane–EtOAc (4:1); the eluates were further examined by chromatography on a Si gel column and/or preparative TLC to give a new hydroxyketone(1) in trace amounts, together with sericealactone and desoxysericealactone (previously isolated from this plant), a pentacyclic triterpene alcohol* 16-hentriacontanone, etc.

(1) mp 83°, gave one spot on TLC (R_f = 0.8 hexane–EtOAc, 17:3); $C_{31}H_{62}O_2$ [analysed and m/e 466 (M^+)]; IR (cm^{-1}) 3150 ~ 3300 (OH), 1700 (CO); PMR (δ ppm) 0.9 (6H, *t*, J = 7 Hz), 1.28 (48H, *br s*,), 2.41 (4H, *t*, J = 7 Hz), 3.6 (1H, *m*).





Oxidation of (1) with Jones reagent afforded a diketone (2); mp 85°, $C_{31}H_{60}O_2$ [*m/e* 464 (M^+)], no OH in IR. MS shows expected fragmentation for assignment as hentriacontone-13,16-dione.

The MS of (1) is complex and we cannot interprete it fully, but from a distinct peak at *m/e* 239, we concluded that the compound is 13-hydroxyhentriacontan-15-one. This conclusion is supported by some other peaks, as shown in the following scheme, along with a peak at *m/e* 58 (characteristic of dialkyl ketones).

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TRANS-2,*CIS*-6-NONADIENAL AND *TRANS*-2-NONENAL IN CUCUMBER FRUITS

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Key Word Index—*Cucumis sativus*; Cucurbitaceae; cucumber fruit; ripening stage; *trans*-2,*cis*-6-nonadienal; *trans*-2-nonenal.

In previous work [1, 2] were reported the biosynthesis of *trans*-2,*cis*-6-nonadienal (1) and *trans*-2-nonenal (2) via *cis*-3,*cis*-6-nonadienal and *cis*-3-nonenal from linolenic and linoleic acids, respectively, using cucumber fruits. The present paper reports the formation of (1) and (2) by homogenates prepared from cucumber fruits at different ripening stages.

As shown in Fig. 1, mid-ripening fruits (300–400 g), which were the harvesting size, produced 1.0–1.6 mg/kg of 1 and *ca* 0.2 mg of 2, while small growing-fruits, less than 250 g in weight, produced only 0.5 mg/kg of 1 and less than 0.1 mg of 2. Thus, the activity of C-9 aldehyde formation was closely related to the ripening stage of the fruits, though the amounts of 1 and 2 were not parallel to ripening stages (fr. wt and fruits length). The amounts of C-6 aldehyde (*trans*-2-hexenal and *n*-hexanal) were less than 10% of C-9 aldehyde in each case.

Substrate specificity for C-9 aldehyde formation is shown in Table 1. Linolenic, linoleic and γ-linolenic acids were converted to the corresponding C-9 aldehydes (1 or 2), but methyl esters of linolenic and linoleic acids were converted to less than 10% of 1 or 2 from free fatty acids. No C-9 aldehydes were produced from triglycerides of linolenic and linoleic acids, oleic, stearic

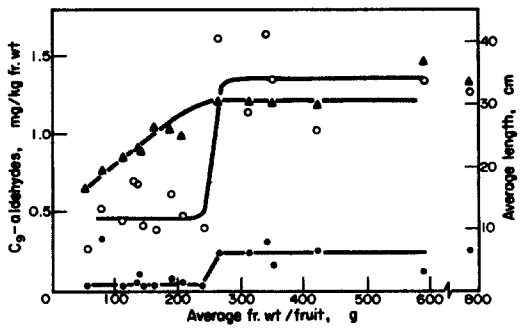

Fig. 1. Formation of *trans*-2,*cis*-6-nonadienal and *trans*-2-nonenal by homogenates of cucumber fruits prepared at different ripening stages. —○—; *trans*-2,*cis*-6-nonadienal (1), —●—; *trans*-2-nonenal (2), —▲—; average length of fruit.