533. *Amides of Vegetable Origin. Part VIII.** *The Constitution and Configuration of the Sanshoöls.*

By L. Crombie and J. L. Tayler.

The insecticidal extract of *Zanthoxylum piperitum* DC. bark contains an unstable lipid *iso*butylamide (m. p. 69°) possessing a conjugated triene system. As Aihara's sanshoöl I is probably an impure form of it, the substance is referred to as α-sanshoöl. On hydrogenation the amide absorbs 4 mols. of hydrogen and gives *N*-*iso*butyldodecanamide. Oxidative degradation yields *N*-*iso*butyloxamic acid, succinic acid, and acetaldehyde, and this, with supporting spectroscopic evidence, shows it to be *N*-*iso*butyldodeca-2 : 6 : 8 : 10-tetraenamide: it appears to be identical with *neo*herculin.

Iodine-catalysed stereomutation of α-sanshoöl gives a higher-melting β-form. Both α- and β-sanshoöl form adducts with maleic anhydride and the spectra of these, and the parent compounds, show that α-sanshoöl has a 2-*trans*-linkage and a *cis*-*trans*-*trans*-triene system, whilst the β-form is all-*trans*. The orientation of the triene unit is demonstrated by oxidising the maleic anhydride adduct of α-sanshoöl to succinic acid. α-Sanshoöl is thus *N*-*iso*butyldodeca-*trans*-2 : *cis*-6 : *trans*-8 : *trans*-10-tetraenamide. Sanshoöl II may be the β-form of this structure.

The lignan (−)-sesamin has been isolated from *Z. piperitum* bark.

Recent synthetical investigation [1] has shown that either sanshoöl I has not the gross structure (I) assigned to it by Aihara,[2] or else it is a very impure substance. Two stereoisomers of (I), *trans*-2 : *trans*-4 : *trans*-8 and *trans*-2 : *trans*-4 : *cis*-8, were synthesised and

$$\mathrm{Me{\cdot}[CH_2]_2{\cdot}CH{=}CH{\cdot}[CH_2]_2{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CO{\cdot}NHBu^i} \quad \text{(I)}$$

it became apparent that further work in this direction would be unrewarding until the natural insecticidal amides of *Zanthoxylum piperitum* DC. had been re-investigated. Through the efforts of Mr. T. Akiyama of the Japanese Embassy in London, a supply of the bark of this tree has become available to us and we now report our findings.

Aihara isolated sanshoöl I by methanol extraction followed by a series of purifications involving three vacuum-distillations.[2] We have used extraction with light petroleum (b. p. 40—60°) followed by partition of the extract with nitromethane. The nitromethane solution was purified, then evaporated *in vacuo*, and the residue chromatographed on neutral alumina from light petroleum and ether. This procedure gave a rapidly eluted fraction containing insecticidal and sialogogue *iso*butylamides and later fractions containing a non-sialogogue crystalline substance, m. p. 121—123°. Aihara [2] reports that he encountered a similar substance but threw no light on its constitution.

The substance of m. p. 121—123° gave analyses correct for $C_{20}H_{18}O_6$ and had ultraviolet maxima at 237 (ε 9100) and 286 mμ (ε 8200). These results suggested that it might

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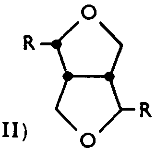
* Part VII, *J.*, 1955, 4244.

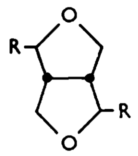
[1] Crombie and Shah, *J.*, 1955, 4244.

[2] Aihara, *J. Pharm. Soc. Japan*, 1950, **70**, 405 [No. 7—8, p. 43]. This paper gives references to the earlier literature; cf. also *idem, ibid.*, 1951, **71**, 1112.

be the lignan (—)-asarinin (II),* which has m. p. 121—122° and ultraviolet maxima at 237 (ε 9300) and 287 mμ (ε 8700),[3] for (—)-asarinin has been isolated from the bark of the related tree *Z. clava-herculis* L.[4, 5] On admixture, however, the m. p. was heavily depressed, and the infrared spectra of the two compounds were very different though no differences in functional groupings could be deduced. The rotation was $[\alpha]_D^{24}$ —65° [(—)-asarinin has $[\alpha]_D^{18}$ —125°], and this led us to suspect that it might be (—)-sesamin (III),† a stereoisomer of (—)-asarinin with m. p. 121—122°, $[\alpha]_D^{18}$ —69°.[6] A specimen of (—)-sesamin was prepared by stereoequilibrating natural (—)-asarinin with alcoholic hydrogen chloride and fractionally crystallising the product.[6] It was identical with the lignan from *Z. piperitum* (mixed m. p. and infrared spectrum). (—)-Sesamin is reported [7] to occur in another natural source, *Asarum sieboldii* Miquel.

(II)





(III)

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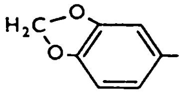

The amide fraction obtained by chromatography was purified by repeated crystallisation and eventually gave a very unstable lipid amide, $C_{16}H_{25}ON$, m. p. 69°, subsequently referred to as α-sanshoöl. When it was hydrogenated over Adams catalyst an octahydro-derivative was produced identical with *N-iso*butyldodecanamide. The infrared spectrum of α-sanshoöl indicated that an α-unsaturated amide function was present and the ultraviolet light absorption (Table 1) gave strong evidence for a conjugated triene system. The ultraviolet data also support the presence of an α-unsaturated amide group as ε at 230 mμ (not a max.) is 12,500 whereas at this wavelength the normal residual absorption of a triene (represented by α-elæostearic acid) is ~4000. *N-iso*Butyldeca-*trans*-2 : *trans*-6-dienamide has ε 10,000 at 230 mμ. A similar conclusion can be drawn from the maleic anhydride adduct of α-sanshoöl in which the triene absorption is destroyed: it has ε 8000 at 230 mμ.

TABLE 1.

	$\lambda_{max.}$ (mμ)	ε
α-Sanshoöl [*cis*-6 : *trans*-8 : *trans*-10]	260	36,000
	269	47,000
	278·5	37,500
α-Elæostearic acid [*cis*-9 : *trans*-11 : *trans*-13] [a]	261	36,000
	271	47,000
	281	38,000
β-Elæostearic acid [*trans*-9 : *trans*-11 : *trans*-13] [a, c]	259	47,000
	268	61,000
	279	49,000
Punicic acid [*cis*-9 : *trans*-11 : *cis*-13] [b]	264	35,000
	274	46,000
	285	34,500

[a] Crombie and Tayler, *J.*, 1954, 2816. [b] Crombie and Jacklin, *J.*, 1957, 1632. [c] The *N-iso*butylamide has maxima at 258, 268, and 278 mμ (ε 42,000, 58,500, and 43,500): see Part IX.

On oxidation with permanganate, *N-iso*butyloxamic acid was isolated, and ozonolysis

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* The geometrical configurations are those assigned by Erdtmann and Pelchowicz (*Chem. and Ind.*, 1955, 567) and Beroza (*J. Amer. Chem. Soc.*, 1956, **78**, 5082); absolute configurations, which are not known, are not to be implied from formulæ (II) and (III).

[3] Aulin-Erdtmann and Erdtmann, *Svensk Papperstidn.*, 1944, **47**, 22.

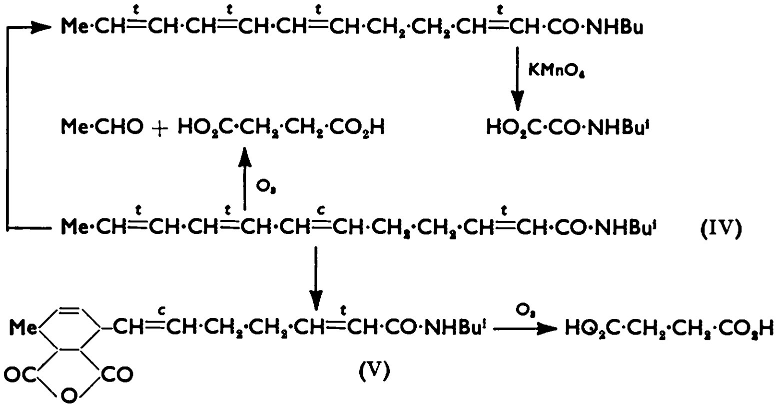
[4] *Inter alia*, Colton, *Amer. J. Pharm.*, 1890, 191; Gordin, *J. Amer. Chem. Soc.*, 1906, **28**, 1648; Dieterle and Schwengler, *Arch. Pharm.*, 1939, **277**, 33.

[5] Crombie, *J.*, 1952, 2997.

[6] Huang-Minlon, *Ber.*, 1937, **70**, 951.

[7] Kaku and Ri, *Keijo J. Med.*, 1938, **9**, 1—4 (*Chem. Abs.*, 1938, **32**, 9089).

gave acetaldehyde (2 : 4-dinitrophenylhydrazone) and succinic acid: the last two fragments were identified by paper chromatographic techniques. Because material was scarce, the permanganate oxidation was actually carried out on the stereoisomeric β-form (see below). It follows that α-sanshoöl is (IV) and its gross structure is the same as that of *neo*herculin.[8] Although direct comparison cannot be made until fresh *neo*herculin has been isolated it is almost certain from m. p.'s and ultraviolet and infrared data, coupled with the similar general behaviour, that the two substances are identical. There also seems a possibility that the lipid *iso*butylamide, echinacein (m. p. 63—64°), recently isolated from *Echinacea angustifolia* DC.,[9] may be the same as α-sanshoöl, for, unless rigorously purified, specimens of the latter (and of *neo*herculin) tend to melt about 5° low. Echinacein gives *N*-*iso*butyldodecanamide on hydrogenation though other degradative evidence is not available beyond the report of a maximum at 259 mμ which is said [9] to be due to a triene system (the other members of the triplet are not mentioned). It is a sialogogue and an insecticide.



(IV)

(V)

Aihara's sanshoöl I,[2] melting near room temperature, seems to have been a very impure specimen of α-sanshoöl. The ultraviolet maximum at 267·5 mμ (ε 33,000), which cannot be due to a 5-monosubstituted *N*-*iso*butylpenta-2 : 4-dienamide type of chromophore as he thought,[1] corresponds to that of an impure triene, and the absence of the bands at 260 and 278·5 mμ, together with the presence of a considerable long-wavelength inflexion, can be accounted for if much impurity were present. Aihara's sample absorbed 3·24 mols. of hydrogen to give *N*-*iso*butyldodecanamide and on oxidative degradation produced *N*-*iso*butyloxamic acid and succinic acid, though the reported *n*-butyric acid is not accounted for.

The configuration of *neo*herculin has been discussed in a previous paper,[8] but, on the data then available, could only be partly defined. The matter has been further examined by using α-sanshoöl. As before, the position of the CH=CH stretching vibration (1668 cm.$^{-1}$, intense because of conjugation with a carboxyamide grouping) suggests that it is a *trans*-structure and further evidence is forthcoming below. Ultraviolet data for the triene linkage (Table 1) indicate that it has probably *cis*-*trans*-*trans*-configuration; on addition of iodine there is a slight shift of the main maximum to 268 mμ and ε increases to 55,000. This parallels the behaviour of α-elæostearic (octadeca-*cis*-9 : *trans*-11 : *trans*-13-trienoic) acid which is similarly isomerised to the β(all-*trans*)-form. Support for validity of this analogy is given by the isolation of a maleic anhydride adduct (V) from α-sanshoöl by reaction in benzene at 100° : this is evidence for two contiguous *trans*-linkages in the triene. An earlier attempt to obtain an adduct from *neo*herculin failed, and on these grounds it had been tentatively proposed that such an arrangement was absent.[8] * β-Sanshoöl also

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* *Added, April 29th*, 1957.—We have since obtained this adduct from *neo*herculin.

[8] Crombie, *J.*, 1955, 995; *Nature*, 1954, **174**, 833.

[9] Jacobson, *Science*, 1954, **120**, 1028.

gives a maleic adduct which, by analogy with β-elæostearic acid, may be a mixture involving addition across both the 6 : 9- and the 8 : 11-positions.[10] The two sanshoöl adducts differ in that the β-form has a band at 967 cm.$^{-1}$ (also present in the maleic adduct of *N*-*iso*butyl-β-elæostearamide at 967 cm.$^{-1}$) which is not found in the α-isomer; this is in the correct position for an unconjugated *trans*-double bond (out-of-plane deformation vibration) and is convincingly ascribed to the double bond of the all-*trans*-triene not involved in adduct formation.[11] In the α-form, this double bond must be *cis*.

Further stereochemical evidence comes from infrared spectra paraffin mull of α- and β-sanshoöl in the 1000—950 cm.$^{-1}$ region. α-Elæostearic acid has bands at 991 and 698 cm.$^{-1}$ characteristic of the *cis*-*trans*-*trans*-triene; on stereomutation these are replaced by a strong band at 987 cm.$^{-1}$. α-Sanshoöl has bands at 994 and 972 cm.$^{-1}$ agreeing with the *cis*-*trans*-*trans*-configuration, but, if our deduction that the 2-unsaturation is *trans* is correct, there ought in any case to be a band at 977 cm.$^{-1}$.[5, 12] Consequently the band at 972 cm.$^{-1}$ should be composite. Evidence that this is so is forthcoming from semiquantitative extinction measurements (carbon tetrachloride solution) as the band is about three times stronger than that of the corresponding band in elæostearic acid. β-Sanshoöl shows the expected all-*trans*-triene band at 996 cm.$^{-1}$ with a strong inflexion at 978 cm.$^{-1}$ which is in the correct position for the *trans*-2-double bond. (This vibration occurs at 977 cm.$^{-1}$ in *N*-*iso*butyldec-*trans*-2-enamide.[5]) It is also significant that the maleic anhydride adducts of α- and β-sanshoöl have bands at 978 (α) and 980 (β) cm.$^{-1}$ which are absent in the adduct from *N*-*iso*butyloctadeca-*trans*-9 : *trans*-11 : *trans*-13-trienamide (no 2-unsaturation): these can be assigned to the above structural feature.

The evidence above determines the position of the olefinic linkages and the configuration of the 2-double bond and the 6 : 8 : 10-triene system in α-sanshoöl. It does not establish the orientation of the *cis*-*trans*-*trans*-system. This was determined by oxidising the maleic anhydride adduct of α-sanshoöl with ozone and hydrogen peroxide. Succinic acid, which could come only from (V), and not from a product of addition to the 6 : 8-linkages, was obtained in 55% yield and detected and estimated by a paper-chromatographic method. The structure (IV), *N*-*iso*butyldodeca-*trans*-2 : *cis*-6 : *trans*-8 : *trans*-10-tetraenamide, agrees with all the known facts about α-sanshoöl.

During the isolation of lipid amides from *Z. piperitum* bark, sanshoöl II, described by Aihara[13] as a very unstable substance softening at 114° and finally melting at 125—126°, was never found. The substance, according to the Japanese author, analyses as $C_{16}H_{25}ON$, absorbs four mols. of hydrogen to give *N*-*iso*butyldodecanamide, and on oxidation yields acetic, succinic, and *N*-*iso*butyloxamic acid. Aihara[13] gave sanshoöl II the structure (VI) but again the light absorption data (max. 267·5 mμ, ε 33,000) are more consistent with

$$\mathrm{Me{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CO{\cdot}NHBu^i} \quad \text{(VI)}$$

an impure conjugated triene than with a 5-monosubstituted *N*-*iso*butylpenta-2 : 4-dienamide (max. 258—259 mμ). Our gross structure (IV) is fully consistent with Aihara's data and we suggest that sanshoöl II may be the β(all-*trans*)-form, obtained by thermal stereomutation of the α-form during the distillation processes. Although we have not been able to spare our best specimens of α-sanshoöl for isomerisation, material of m. p. 63—66° has given β-form of m. p. 110—115° on irradiation in the presence of a trace of iodine. The substance, although crystallising in rosettes of excellent needles, is unstable and very difficult to purify. We have never handled a pure sample, and spectroscopic data obtained on the β-form were obtained with the above material. When the crude crystallisation residues from α-sanshoöl preparations were treated with iodine, considerable amounts of still less pure β-form could be isolated. The *N*-*iso*butyldodecanamide formed

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[10] Bickford, Dupré, Mack, and O'Connor, *J. Amer. Oil Chemists' Soc.*, 1953, **30**, 376.

[11] Cf. Paschke, Tolberg, and Wheeler, *ibid.*, 1953, **30**, 97.

[12] Crombie, *J.*, 1952, 4338.

[13] Aihara, *J. Pharm. Soc. Japan*, 1950, **70**, 409 [No. 7—8, p. 47].

from the latter by hydrogenation is not completely pure, and contamination by amides of different chain length seems to be involved. On ozonolysis the crude β-material gave mainly acetaldehyde together with smaller amounts of longer-chain aldehydes.

EXPERIMENTAL

Analyses were carried out in the Microanalytical (Miss J. Cuckney) and infrared measurements in the Spectroscopic Laboratories (Mr. R. L. Erskine) of this Department. A Grubb-Parsons double-beam instrument with rock-salt optics was used. Unless otherwise stated, solid substances were examined as paraffin mulls. Ultraviolet absorption data were obtained with pure ethanol as solvent.

Isolation of α-Sanshoöl and (−)-Sesamin.—Ground bark of *Z. piperitum* (2·7 kg.) was extracted with light petroleum (b. p. 40—60°) in a semicontinuous process in which, after soaking (24 hr.) the extract was drawn off into a pot and two-thirds of the petroleum redistilled into the extractor. Eight such soakings were given and heating of the extracts kept to a minimum. The greenish-yellow total extract remaining in the pot was concentrated to 1 l. and partitioned with portions of nitromethane (1 × 300, 1 × 200, and 5 × 100 ml.). Evaporation of the greenish-yellow nitromethane extract under reduced pressure gave a dark green oil which was dissolved in ether (300 ml.) and washed with 2N-sodium hydroxide, 2N-sulphuric acid, and then water. The ethereal solution was dried (Na_2SO_4) at 3°, and evaporated to a greenish oil (33 g., 1·2%) (Aihara[3] found 1·1% of methanol extractive).

The oil was dissolved in 1 : 1 light petroleum (b. p. 40—60°)–ether and chromatographed on neutral alumina. The fractions which were rapidly eluted contained lipid *iso*butylamides and their progress could be followed from the sialogogue effect of material leaving the column. After evaporation, this group of fractions was crystallised four times, with cooling, where necessary, to sub-zero temperatures, to give impure α-sanshoöl (717 mg., 0·03%), m. p. 63—66°. The next group of fractions was set aside at 0° for several days and deposited crude (−)-sesamin (1 g., 0·04%) which had m. p. 120° (sintering from 84°), raised by repeated crystallisation from ethanol to m. p. 121—123°. The substance was not a sialogogue. Later fractions from the chromatogram (eluted with pure ether) yielded a yellow oil (1 g.) which was not a sialogogue and was not examined further.

When the residues from the crystallisation of α-sanshoöl were treated under light petroleum with iodine, crude β-sanshoöl (3 g.), m. p. 98° (unsharp), crystallised. The β-form was not encountered at any other stage of the working-up procedure. The crystallisation residues, before isomerisation, gave a 56% kill when tested against *Tenebrio molitor* as a 3% w/v solution according to a standard measured-drop technique.

α-Sanshoöl.—Repeated crystallisation of the crude product (above) from light petroleum (b. p. 40—60°) gave α-sanshoöl of m. p. 69°, separating from solution in a characteristic bulky form. *neo*Herculin has m. p. 69—70° and crystallises similarly[8] (Found : C, 77·85; H, 10·25; N, 5·65. Calc. for $C_{16}H_{25}ON$: C, 77·7; H, 10·2; N, 5·65%). Microhydrogenation 3·85 H_2. Light absorption see Table 1. Infrared bands were present at 3200m and 3060w (NH), 1668m (α-C=C), 1626s (amide carbonyl), 1560 (amide B), 994, and 972 cm.$^{-1}$ (*trans-trans-cis*-triene and *trans*-α-CH=CH). In carbon tetrachloride solution the apparent extinction coefficients at 992 and 964 cm.$^{-1}$ were 275 and 110 respectively. See Crombie and Jacklin[14] for comparative data. The m. p. of 69° above refers to the best sample obtained: others had m. p. 65—67° even after a considerable number of crystallisations. α-Sanshoöl must be kept sealed *in vacuo* at 0°. A 3% w/v solution, when tested against *T. molitor* by the above technique, gave a 77% kill.

β-Sanshoöl.—α-Sanshoöl (217 mg.; m. p. 63—66°) was dissolved in light petroleum (b. p. 40—60°; 20 ml.), a trace of iodine added, and the solution illuminated with a tungsten lamp. The crude β-form (200 mg.) crystallised in small needles of excellent form and after two crystallisations had m. p. 112°. Other samples of α-sanshoöl of similar quality gave products of m. p. 110—115° : the m. p. was not readily improved by crystallisation and in some cases deteriorated (Found : C, 77·15; H, 10·0; N, 5·6%). Light absorption max. 259, 267·5, and 278 mμ (ε 38,500,

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[14] Crombie and Jacklin, *J.*, 1957, 1632.

48,500, and 39,000). Infrared bands: 3250m and 3060w (NH), 1667m (α-C=C), 1623s (amide carbonyl), 1549ms (amide B), 996s (all-*trans*-triene), and 978 cm.$^{-1}$ strong inflexion (*trans*-α-CH=CH). The β-form is a weaker sialogogue than the α-form: a 3% w/v solution in acetone, when tested against *T. molitor* as above, gave a 21% kill.

Hydrogenation of α-Sanshoöl.—The amide (209 mg.) was hydrogenated in ethyl acetate with 5% palladised carbon as catalyst: almost exactly 4 mols. of hydrogen were absorbed. The catalyst was filtered off and the solution evaporated, to give a solid, m. p. 48—49°, which when recrystallised from light petroleum (b. p. 60—80°) gave *N-iso*butyldodecanamide, m. p. 51—52·5°, undepressed by an authentic specimen of m. p. 51·5—53°.

Under similar conditions, crude β-sanshoöl (m. p. 103—112°; obtained by recrystallising β-material obtained from the crystallisation residues from the α-form) absorbed almost exactly 4 mol. of hydrogen. The product had m. p. 45—47° but the m. p. was not improved by five crystallisations. On admixture with *N-iso*butyldodecanamide, the m. p. was raised to 47—50°.

Oxidation Products of Sanshoöl.—(a) *Succinic acid.* α-Sanshoöl (49 mg.) was ozonised in glacial acetic acid (90 min.), 30% hydrogen peroxide (1·5 ml.) added, and the mixture set aside at 35° (2 days).[15] Water (20 ml.) was added and the solution extracted with light petroleum and then chloroform. The aqueous phase was carefully evaporated to dryness, the residue (oily solid) dissolved in ethanol, and a portion chromatographed on paper sheet according to the method of Cheftel and his co-workers [16] (development, ammoniacal ethanol: spraying reagents, bromocresol-green–lead acetate). A mixture of oxalic, malonic, and succinic acid was run on the same sheet for reference. Only one prominent spot, corresponding in R_F value to the succinic acid standard, was observed.

(b) *Acetaldehyde.* α-Sanshoöl (183 mg.) was ozonised in "AnalaR" glacial acetic acid (5 ml.) for 80 min. Zinc dust (2 g.) and water (30 ml.) were added, the mixture was heated to the b. p., and volatile aldehydes were steam-distilled into Brady's reagent. The precipitated 2 : 4-dinitrophenylhydrazone was filtered off, dissolved in benzene, and chromatographed on alumina (Brockmann grade III). The weakly absorbed zone was eluted; the 2 : 4-dinitrophenylhydrazone (30 mg.) recovered had m. p. 151°, raised by crystallisations to 158—160°. For identification, the derivative was chromatographed on paper sheet impregnated with olive oil, with *iso*propanol–water as the eluting solvent, according to Seligman and Edmonds's method.[17] The 2 : 4-dinitrophenylhydrazones of formaldehyde, acetaldehyde, and propionaldehyde were chromatographed as reference substances. Only one prominent spot, corresponding to acetaldehyde 2 : 4-dinitrophenylhydrazone, was obtained though traces of two other 2 : 4-dinitrophenylhydrazones were noted. When ozonised by the same technique, crude β-sanshoöl (above) gave mainly acetaldehyde together with small amounts of higher aldehydes.

(c) N-iso*Butyloxamic acid.* Crude β-sanshoöl (445 mg.) was dissolved in aqueous acetone, and potassium permanganate (3 g.) added with shaking, at 50°. The product was filtered, concentrated, acidified, and steam-distilled to remove volatile acids. After neutralisation, the residue from the steam-distillation was concentrated to 50 ml. and then acidified and continuously extracted with ether. The extract was evaporated to a gummy solid from which *N-iso*butyloxamic acid was isolated by treatment with portions of hot light petroleum (b. p. 40—60°). The *N-iso*butyloxamic acid crystallised in white feathery needles, m. p. 104—106°, undepressed when admixed with an authentic specimen of m. p. 105—107°.

Maleic Anhydride Adduct of α-Sanshoöl.—α-Sanshoöl (326 mg.), maleic anhydride (130 mg.), and benzene (4 ml.) were mixed (a yellow colour developed at once) and heated in a sealed tube at 100° for 24 hr. On cooling, no crystals were deposited, so the benzene was evaporated leaving a yellow oil which solidified when triturated with ether and light petroleum (b. p. 60—80°). The white solid (273 mg.; m. p. 90—92°) was crystallised from ether–light petroleum to m. p. 99—100·5°: the *adduct* had a powdery appearance (Found: N, 3·95. $C_{20}H_{27}O_4N$ requires N, 4·05%). No high-intensity maximum was observed in the ultraviolet region above 210 mμ (ε values at 210 and 230 mμ were 16,000 and 8000). *N-iso*Butyldeca-*trans*-2 : *trans*-6-dienamide also showed no maximum in this range when examined with a photoelectric instrument (ε values at 210 and 230 mμ were 20,500 and 10,000). Previously, when the photographic method (Hilger medium quartz instrument) was used, a subsidiary maximum at 226 mμ on a rising curve was reported [5] for this and related α-unsaturated *iso*butylamides. For

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[15] Cf. Klenk and Bongard, *Z. physiol. Chem.*, 1952, **290**, 181.

[16] Cheftel, Munier, and Macheboeuf, *Bull. Soc. Chim. biol.*, 1952, **34**, 380.

[17] Seligman and Edmonds, *Chem. and Ind.*, 1955, 1406.

comments on similar discrepancies see Allan *et al.*[18] The infrared spectrum of α-sanshoöl–maleic anhydride adduct showed bands at 3295m and 3125w (NH), 1838mw and 1765s (anhydride), 1669m (α-C=C), 1618s (amide-carbonyl), 1543m (amide B) and 978m cm.$^{-1}$ (*trans*-α-CH=CH).

Under similar conditions β-sanshoöl gave an adduct which, after three crystallisations from ethyl acetate–light petroleum (b. p. 40—60°) or benzene–light petroleum, had m. p. 148—151° (Found: N, 3·9%). Infrared bands were present at 3280m and 3040w (NH), 1842m and 1768s (acid anhydride), 1664m (α-C=C), 1618s (α-unsaturated amide carbonyl), 1547m (amide B), 980m (*trans*-α-CH=CH), and 967m cm.$^{-1}$ (unconjugated *trans*-CH=CH). Compare the maleic adduct of *N*-*iso*butyloctadeca-*trans*-9 : *trans*-11-*trans*-13-trienamide which has bands at 1843m and 1770s (acid anhydride), 1645s (α-saturated amide carbonyl), 1547s (amide B), and 967m cm.$^{-1}$ (unconjugated *trans*-CH=CH).

Oxidation of α-*Sanshoöl–Maleic Anhydride Adduct.*—The maleic adduct (80 mg.) was ozonised for 1 hr. in glacial acetic acid, and the product treated with 30% hydrogen peroxide at 35° (48 hr.). The solution was concentrated, diluted and extracted with light petroleum (b. p. 40—60°) and then chloroform. The aqueous phase was evaporated under a vacuum, the residue dissolved in a known volume of ethanol, and an aliquot part chromatographed by the method of Cheftel *et al.*[16] Succinic acid was identified (~55% yield as determined by a spot-area technique [19]). A second large spot of R_F near to that of malonic acid was identified: since no malonic acid was obtained from α-sanshoöl itself, the spot is probably due to an acid formed by degradation of the *cyclo*hexane ring. It was not *N*-*iso*butyloxamic acid as the latter has an R_F value greater than that of succinic acid.

Identification of (−)-*Sesamin.*—(−)-Sesamin obtained from *Z. piperitum* bark had m. p. 121—123°, $[\alpha]_D^{24}$ −65° (*c*, 2·67% in $CHCl_3$) [Found: C, 67·55; H, 5·4; O (direct) 27·3%; *M* (Rast), 335. Calc. for $C_{20}H_{18}O_6$: C, 67·75; H, 5·1; O, 27·1%; *M*, 354·3]. See text for ultraviolet data. On admixture with (−)-asarinin the m. p. was depressed to 98—103°.

(−)-Asarinin, isolated from *Z. clava-herculis* bark,[5] had m. p. 121°, $[\alpha]_D^{21}$ −125° (*c* 2·90% in $CHCl_3$). The substance (5 g.) was stereoequilibrated according to Huang-Minlon's directions [6] under reflux (12 hr.) with 10% alcoholic hydrogen chloride. By fractional crystallisation of the product, (−)-sesamin, m. p. 120°, was isolated: it did not depress the m. p. of the above specimen and had an identical infrared spectrum. Recorded data [6] are m. p. 121—122°, $[\alpha]_D^{18}$ −68·9° (*c* 1·14% in $CHCl_3$).

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[18] Allan, Jones, and Whiting, *J.*, 1955, 1862.

[19] Ackman, Linstead, and Weedon, unpublished work.