## 574. *Amides of Vegetable Origin. Part I. Stereoisomeric* N-iso*Butyl-undeca*-1 : 7-*diene*-1-*carboxyamides and the Structure of Herculin.*

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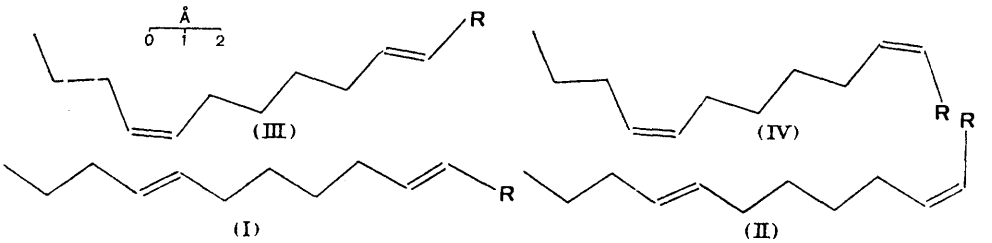
Syntheses of the *trans*-1 : *trans*-7- and *cis*-1 : *trans*-7-stereoisomers of *N-iso*butylundeca-1 : 7-diene-1-carboxyamides are recorded. The assigned configurations of these and the two other possible geometrical isomers, previously described, are supported by consideration of their infra-red spectra. None of them is identical with herculin which has therefore been assigned a wrong gross structure (stereochemistry undefined). Attempted re-isolation of herculin from the bark of *Xanthoxylum clava-herculis* L. failed, though from the cognate fraction a monosubstituted amide was obtained with certain properties similar to those recorded for the former. The new compound is more unsaturated than herculin as its ultra-violet spectrum reveals conjugated triethenoid unsaturation, and it is named *neo*herculin. The question of the nature of herculin remains open.

Several aliphatic *iso*butylamides have been isolated from vegetable sources by various authors. Amongst the better known are pellitorine obtained from the roots of *Anacyclus pyrethrum* DC. (Gulland and Hopton, *J.*, 1930, 6; Jacobson, *J. Amer. Chem. Soc.*, 1949, **71**, 366), herculin from the bark of *Xanthoxylum clava-herculis* L. (Jacobson, *ibid.*, 1948, **70**, 4234), affinin from the roots of *Heliopsis longipes* A. Gray (Acree, Jacobson, and Haller,

*J. Org. Chem.*, 1945, **10**, 236, 449), and scabrin from the roots of *Heliopsis scabra* Dunal. (Jacobson, *J. Amer. Chem. Soc.*, 1951, **73**, 100). Spilanthol has been isolated from the flowers of *Spilanthes oleracea* Jacquin and *Spilanthes acmella* (Asano and Kanematsu, *Ber.*, 1932, **65**, 1602; Gokhale and Bide, *J. Indian Chem. Soc.*, 1945, **22**, 250), whilst Japanese investigators have separated two aliphatic *iso*butylamides, shanshoöls I and II, from the fruits and bark of *Xanthoxylum piperitum* DC. (Murayama and Shinozaki, *J. Pharm. Soc. Japan*, 1931, **51**, 379; Aihiara, *ibid.*, 1950, **70**, 43, 47). There is scattered evidence that, as judged from the properties of the crude plant extracts, a number of similar compounds is to be found in other species of these genera. All the compounds mentioned have a characteristic pungent taste: when placed on the tongue a tingling sensation is caused accompanied by profuse salivation. Interest in them has quickened since several have been shown to possess considerable insecticidal activity, sometimes surpassing that of the pyrethrins (against houseflies). Structural investigation within the group is incomplete but all those known are *iso*butylamides of acids containing an unbranched sequence of ten, twelve, or eighteen carbon atoms with two or more double bonds. They are unstable in air at room temperature, though less so in solution.

None of the structures proposed for these compounds has been confirmed by synthesis, and their stereochemistry is unknown in all cases. The investigation described in this paper was aimed at verifying the proposed gross structure for herculin * (Jacobson, *loc. cit.*), *N-iso*butylundeca-1 : 7-diene-1-carboxyamide, and elucidating its stereochemistry by preparation of the four possible isomers, *viz.*: *trans*-1 : *trans*-7 (I*a*), *cis*-1 : *trans*-7 (II*a*), *trans*-1 : *cis*-7 (III*a*), and *cis*-1 : *cis*-7 (IV*a*). During this work preparation of the *trans*-1 : *cis*-7- and the *cis*-1 : *cis*-7-compound was reported (Raphael and Sondheimer, *J.*, 1950, 115; 1951, 2693), so attention was concentrated on synthesis of the remaining pair and on examination of the four compounds to confirm their stereochemistry and relate them to natural herculin.

As the key synthetical intermediate *trans-n*-non-5-en-1-ol was required. Oct-4-en-1-ol can be prepared in excellent yield by the ring scission of the readily available 3-chlorotetrahydro-2-*n*-propylpyran with metallic sodium and is known to have the *trans*-configuration (Riobé, *Ann. Chim.*, 1949, **4**, 593; Crombie and Harper, *J.*, 1950, 1707).



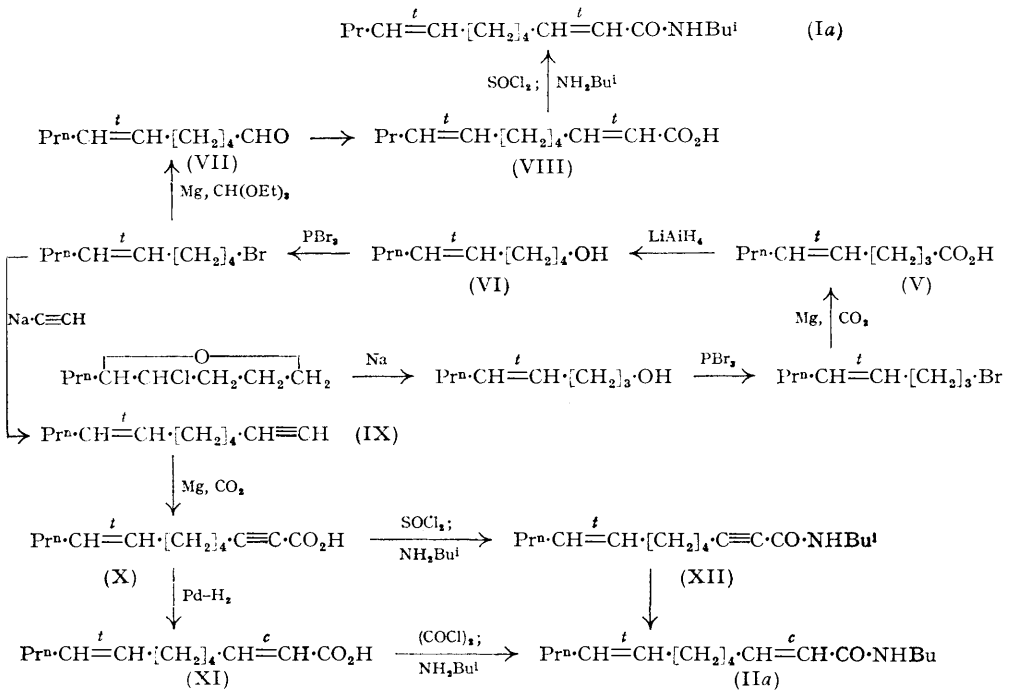

(*a*) R = ·CO·NH·$CH_2$·$CHMe_2$ (*b*) R = ·$CO_2^-$ $C(NH_2)(=NH_2^+)$·S·$CH_2$Ph

By a standard homologation procedure this alcohol was converted *via* its bromide and the derived Grignard reagent into *trans-n*-oct-4-ene-1-carboxylic acid (V) (*S*-benzylthiuronium salt) which was reduced with lithium aluminium hydride to *trans-n*-non-5-en-1-ol (VI) (*p*-diphenylylurethane), the overall yield being 47%.

For the preparation of undeca-*trans*-1 : *trans*-7-diene-1-carboxylic acid, the nonenol was converted into its bromide with phosphorus tribromide, and the derived Grignard reagent treated with ethyl orthoformate. Hydrolysis of the resultant acetal yielded *trans-n*-non-5-en-1-al (VII) (2 : 4-dinitrophenylhydrazone), purified by means of its bisulphite compound. This aldehyde condensed with malonic acid in pyridine at room temperature during five days, to give the required diene acid (VIII) (*S*-benzylthiuronium salt) which

* To avoid confusion it is pointed out that the source of herculin, *Xanthoxylum clava-herculis* L., is also referred to in the literature as *X. carolinianum* Lam., *Fagara caroliniana* Engler, southern prickly ash, Hercules club, and toothache tree.

crystallised in colourless plates when distilled. Evidence that a double bond introduced into an acid by means of the Doebner reaction has the *trans*-configuration has been cited by numerous authors (von Auwers and Wissenbach, *Ber.*, 1923, **56**, 715; Letch and Linstead,




*J.*, 1932, 443; Schjanberg, *Ber.*, 1937, **70**, 2385; Lauer and Gensler, *J. Amer. Chem. Soc.*, 1945, **57**, 1171). On the other hand Joly and Amiard (*Bull. Soc. chim.*, 1947, 139) state that, dependent on conditions, 6—17% of (*cis*-)hexenolactone can be isolated in the preparation of sorbic acid by this reaction, though this of course does not *necessitate* a *cis*-αβ-precursor. In the present instance the crystallinity of the purified acid indicates the absence of *cis*-contaminant. When treated with thionyl chloride and an excess of *iso*butylamine, *N-iso*butylundeca-*trans*-1 : *trans*-7-diene-1-carboxyamide (I*a*) was formed which when distilled crystallised in waxy needles, m. p. 54°.

The *cis* : *cis*-isomer was prepared as follows. *trans-n*-Non-5-enyl bromide was converted into *trans*-undeca-7-ene-1-yne (IX) by condensation with sodium acetylide, and the Grignard complex of the latter carboxylated at atmospheric pressure in ether with solid carbon dioxide. Catalytic semi-hydrogenation of the acetylenic linkage of the enyne acid (X) thus prepared yielded undeca-*cis*-1 : *trans*-7-diene-1-carboxylic acid (XI) (*S*-benzylthiuronium salt). The latter was converted into its chloride by oxalyl chloride under mild conditions. This was not purified but was converted directly into *N-iso*butylundeca-*cis*-1 : *trans*-7-diene-1-carboxyamide (II*a*) which proved to be a liquid. A second specimen was prepared by proceeding from the enyne acid (X) to its *iso*butylamide (XII) and then semi-hydrogenating the triple bond. The assumption that the catalysed semi-hydrogenation step yields an essentially *cis*-isomer is founded on an extensive literature to this effect (for summaries see Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 77; Crombie, *Quart. Reviews*, 1952, **6**, 101). But there is no doubt that a small proportion of the *trans*-compound is often found, probably by the subsequent stereomutation on the catalyst of the *cis*-compound already formed (Farkas and Farkas, *Trans. Faraday Soc.*, 1937, **33**, 837). Its presence has been revealed by cryoscopic measurement and by Raman and infra-red spectroscopic measurement (Henne and Greenlee, *J. Amer. Chem. Soc.*, 1943, **65**, 2020; Sondheimer, *J.*, 1950, 877; G. Smets, *Acad. Roy. Belg., Classe Sci.*, 1947, **21**, 3). The level

of contamination doubtless varies with the conditions and speed of hydrogenation but the conditions used here have previously enabled *cis*-compounds to be synthesised and proved identical with natural materials (*e.g.*, Crombie and Harper, *J.*, 1950, 1152) without interference by *trans*-impurity.

Data for the undeca-1 : 7-diene-1-carboxylic acids and their derivatives are listed in Table 1. Small specimens of the *trans*-1 : *cis*-7- and *cis*-1 : *cis*-7-*iso*butylamides were generously made available by Drs. Raphael and Sondheimer and were used to obtain certain

TABLE 1. *Undecadiene-1-carboxylic acids and derivatives.*

| | | | *S*-Bzthu,* | *N-iso*Butylamides | | No. of |
|---|---|---|---|---|---|---|
| | B. p./mm. | $n_D^{20}$ | m. p. | B. p./mm. | $n_D^{20}$† | C:C |
| *trans*-1 : *trans*-7- (I) ‡... | 137°/0·7 | 1·4734 [1] | 159° | 145°/4 × $10^{-3}$ | [m. p. 54°] | 1·95 |
| *cis*-1 : *trans*-7- (II) ‡ ... | 115—117°/0·5 | 1·4699 | 148 | 142°/3 × $10^{-2}$ | 1·4824 | 1·91 |
| *trans*-1 : *cis*-7- [2] (III) ‡ | 98—100°/$10^{-5}$ | 1·4710 | 143—144 | 133—135°/$10^{-5}$ | 1·4806 | — |
| *cis*-1 : *cis*-7- [3] (IV) ‡ ... | 108—109°/$10^{-4}$ | 1·4741 | 129—130 | 145—146°/$10^{-2}$ | 1·4830 | 1·81 [4] |

[1] M. p. 35°. [2] Data by Raphael and Sondheimer, *J.*, 1951, 2693. [3] Data by Raphael and Sondheimer, *J.*, 1950, 115. [4] New data obtained in the present work.
* *S*-Benzylthiuronium salt. † Adjusted to 20° by −0·0004 per degree within a range of ±5°.
‡ R = $CO_2H$.

TABLE 2. *Ultra-violet light absorption data.*[1]

| | $\lambda_{max.}$, mμ | $\varepsilon_{max.}$ |
|---|---|---|
| $Pr^n$·CH=CH·$[CH_2]_4$·CH=CH·CO·NHBu. | | |
| *trans*-1 : *trans*-7- (I*a*) | 226 | 11,500 |
| *cis*-1 : *trans*-7- (II*a*) | 226 | 10,700 |
| *trans*-1 : *cis*-7 (III*a*) | 227 | 10,500 |
| *cis*-1 : *cis*-7- (IV*a*) | 227 | 8,700 |
| *trans*-Me·$[CH_2]_6$·CH=CH·CO·NHBu$^i$ | 226 | 10,300 |
| *cis*- ,, ,, ,, | 226 | 10,000 |
| Me·$[CH_2]_8$·CO·NHBu$^i$ | < 215 | — |
| | (λ 215 | ε 1,000) |
| *trans*-Me·$[CH_2]_6$·CH=CH·$CO_2$H | < 215 | — |
| | { λ 230 | ε 3,400 } |
| | { λ 215 | ε 11,900 } |
| *trans*-Me·CH=CH·$CO_2$H [2] | 205 | 15,700 |
| ,, Me·CH=CH·CO·$NH_2$ | < 216 | — |
| | { λ 216 | ε 12,000 } |
| | { λ 230 | ε 4,000 } |
| ,, Me·CH=CH·CO·NHBu$^i$ | 227 | 8,500 |
| ,, Me·CH=CH·CO·$NEt_2$ [3] | 215 | 11,000 |

[1] Data obtained with ethanol as solvent. [2] C. J. Timmons, private communication. [3] Bowden Braude, and Jones, *J.*, 1946, 948.

new data recorded here. The carbon skeletons of the two stereoisomers prepared in the present work were demonstrated by hydrogenation of the diene acids to lauric acid.

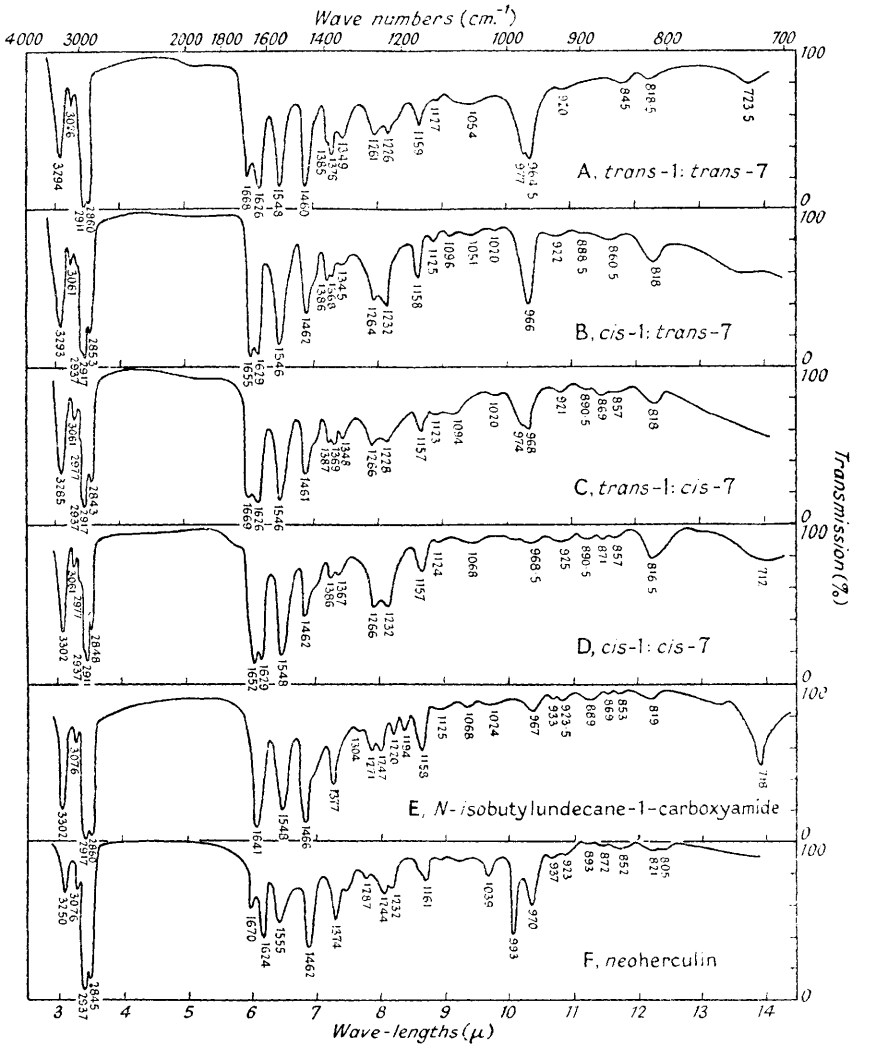
The melting points of the four *S*-benzylthiuronium salts of the undecadiene-1-carboxylic acids (Table 1) support the claim that they have the stereochemical structures assigned to them. These decrease as the bending of the chain increases [*i.e.*, m. p. of *trans*-1 : *trans*-7 (I*b*) > *cis*-1 : *trans*-7 (II*b*) > *trans*-1 : *cis*-7 (III*b*) > *cis*-1 : *cis*-7 (IV*b*)]. In a qualitative sense it is known that the more linear members of a comparable series of molecules pack more readily and therefore form more stable crystal lattices which have higher melting points.

The ultra-violet light absorption of all four stereoisomeric *iso*butylamides (Table 2) showed a maximum on a rising curve at 226 mμ. with an extinction coefficient of ~10,000. Such a maximum, whilst present in other αβ-unsaturated *iso*butylamides was absent in the saturated compounds. In the crotonic acid series it was noted that the *iso*butylamide maximum was at a wave-length longer than that of either the amide or the diethylamide. As regards geometrical isomerism, in such cases as the present where there is no steric hindrance to the planarity of the chromophore and where its length is the same in both the *cis*- and the *trans*-form (on the assumption that the preferred *s*-configuration about the intervening single bond is the same in both cases), current theory indicates that the ultra-violet light absorption of the isomers should be very similar. The variation in $\lambda_{max.}$ for the four stereoisomers is negligible (1 mμ) and, though the values of $\varepsilon_{max.}$ are not identical

within the limits of experimental error, it would be imprudent to draw conclusions on the present data alone, particularly since the low figure for the *cis* : *cis*-isomer may be associated with its low hydrogenation value (C:C, Table 1).

In order to gain further evidence of the discrete nature of the isomers and to support their assigned configurations the infra-red spectra of the *N-iso*butylundecadiene-1-carboxyamides have been examined (Fig. 1). The saturated isomer is included for comparison.

FIG. 1. *Infra-red spectra of* N-iso*butylundeca*-1 : 7-*diene*-1-*carboxyamides and related compounds.*




(*B*—*D*, liquid films; *A*, *E*, *F*, paraffin mulls, paraffin absorption present.)

The spectra, which are of pure liquid films or paraffin mulls of the material and are therefore influenced by intermolecular hydrogen bonding, show the usual features for monosubstituted amides. In the four stereoisomers the N–H stretching frequency is present at 3285—3302 cm.$^{-1}$, the amide band A (carbonyl) at 1626—1629 cm.$^{-1}$, and the amide band B—which is in the position characteristic of a monosubstituted amide—at 1546—1548 cm.$^{-1}$ (Richards and Thompson, *J.*, 1947, 1248; Randall, Fowler, Fuson, and Dangl, " Infra-Red Determination of Organic Structures," D. Van Nostrand, New York, 1949; Fuson, Josien, and Powell, *J. Amer. Chem. Soc.*, 1952, **74**, 1; and references cited in these works).

Conjugation displaces the carbonyl absorption to lower frequencies by some 10—15 cm.$^{-1}$ in the *iso*butylamides and the free acids (Table 3). In part as a consequence of the importance of the resonance form $R\cdot CH{=}CH\cdot C\overset{O^-}{\underset{NHBu^i}{\leqslant}}$ to the secondary amide structure (cf. Pauling, Corey, and Branson, *Proc. Nat. Acad. Sci.*, 1951, **37**, 205; *X*-ray crystallography indicates some 50% of double bond character for the carbon–nitrogen linkage, and the amide group is considered to be planar), the carbonyl frequency falls by some 70 cm.$^{-1}$ with respect to the corresponding ketone (or dimeric acid). The small peak at 3061—3076 cm.$^{-1}$ appears consistently in the spectra of the compounds.

In order to facilitate further interpretation of the spectra certain model compounds were examined (Table 3). Of those not mentioned above, *trans*-non-1-ene-1-carboxylic

TABLE 3. *Infra-red absorption maxima (cm.$^{-1}$).*

| | C=O, stretch | C=C, stretch | C=C—H bend |
|---|---|---|---|
| $Me\cdot[CH_2]_{10}\cdot CO_2H$ * | 1711 | — | — |
| *cis*-$Et\cdot CH{=}CH\cdot[CH_2]_2\cdot CO_2H$ | 1714 | — | — [1] |
| *trans*- ,, ,, | 1714 | — | 966·5 |
| *cis*-$Bu^n\cdot CH{=}CH\cdot CO_2H$ | 1702 | 1642 | — [1] |
| *trans*- ,, | 1702 | 1652 | 984 |
| *cis*-1:*trans*-7-$Pr^n\cdot CH{=}CH\cdot[CH_2]_4\cdot CH{=}CH\cdot CO_2H$ | 1698 | 1642 | 966 |
| *trans*-1 : *trans*-7- ,, ,, ,, * | 1700 | 1652 | 966·5, 979 [2] |
| *trans*-$Pr^n\cdot CH{=}CH\cdot[CH_2]_4\cdot OH$ | — | — | 966·5 |
| ,, $Me\cdot[CH_2]_{10}\cdot CO\cdot NHBu^i$ * | 1642 | — | — |
| *cis*-$Me\cdot[CH_2]_6\cdot CH{=}CH\cdot CO\cdot NHBu^i$ | 1631 | 1660 | — |
| *trans*- ,, ,, * | 1629 | 1671 | 977 |
| ,, $Me\cdot[CH_2]_6\cdot C{\equiv}C\cdot CO\cdot NHBu^i$ | 1634 | 2257,[2] 2248, 2230 | — |

[1] Faint absorption at the wave-length characteristic of the *trans*-isomer (probably contamination, see text). [2] Shoulder. [3] Wotiz and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 3441, give 2190—2260 cm.$^{-1}$ (plus nearby satellites) for the R—C≡C—R stretching frequency. The complexity is said to be due to overtones or combination tones whose intensity has been enhanced by resonance with the fundamental. * Paraffin mull; others pure liquid films.

acid was made from *n*-octaldehyde by the Doebner reaction and its *iso*butylamide prepared in the usual way. Non-1-yne-1-carboxylic acid was made by carboxylation of non-1-ynylmagnesium bromide. This was converted into its *iso*butylamide and the latter semi-hydrogenated to *N-iso*butyl-*cis*-non-1-ene-1-carboxyamide. *cis*- and *trans*-Hept-2-enoic and -hept-4-enoic acids were available from other work (Crombie and Harper, unpublished).

Attention was first focused on the spectral region near 1000 cm.$^{-1}$. It is now well established that absorption at 966 cm.$^{-1}$ (10·35 μ) is characteristic of a *trans*-double bond in the environment $-CH_2\cdot CH{=}CH\cdot CH_2-$. The absorption is considered to be due to the unsaturated C–H deformation and is not present in the *cis*-isomers (Rasmussen, Brattain, and Zuco, *J. Chem. Phys.*, 1947, **15**, 135; Sheppard and Sutherland, *Proc. Roy. Soc., A*, 1949, **196**, 195; Crombie and Harper, *J.*, 1950, 873; for more extensive references see Crombie, *Quart. Reviews*, 1952, **6**, 101). Examination of the model compounds showed that the frequency was sensitive to the influence of conjugation on the carbon–carbon double bond. In both the *trans*-αβ-unsaturated acids and the *iso*butylamides there was a shift to higher frequencies of 12—18 cm.$^{-1}$. Absorption was again absent or very weak in the corresponding *cis*-isomers.

Considering now the spectra of the *N-iso*butylundeca-1 : 7-diene-1-carboxyamides in this region, the absorption at 977 and 965 cm.$^{-1}$ (Fig. 2) in the *trans*-1 : *trans*-7-isomer can be assigned to the C–H deformation frequency at the *trans*-1- and the *trans*-7-double bonds respectively. As expected, the *cis*-1 : *cis*-7-isomer has only weak absorption here and this is probably due to traces of stereoisomeric impurities. Similarly the *cis*-1 : *trans*-7-compound has only one absorption band and this at 966 cm.$^{-1}$ due to the *trans*-7-unsaturation. It would be predicted that the *trans*-1 : *cis*-7-diene *iso*butylamide should have but one absorption maximum in the C=C–H deformation region, and this at ~978 cm.$^{-1}$. The compound does in fact have a strong inflexion at 974 cm.$^{-1}$ but there is maximal absorption at 968 cm.$^{-1}$ (Fig. 2). This is interpreted as indicating the presence of some *trans*-stereoisomeric impurity which may have arisen during the semi-hydrogenation step involved in

its preparation * (Raphael and Sondheimer, *loc. cit.*). The position of the frequency corresponding with the C–H deformation about a *cis*-double bond is uncertain, though it is generally agreed to be lower than the *trans*. In this connection it may be noted that a band (818·5—816·5 cm.$^{-1}$) already present in the saturated and the *trans* : *trans*-compound is reinforced as one passes through the *cis* : *trans*- to the *cis* : *cis*-isomers.

In the C=C stretching region it was noted that the two diene *iso*butylamides with *cis*-1-double bonds has this vibration frequency at 1652 and 1655 cm.$^{-1}$ whilst the pair with *trans*-1-unsaturation showed it at 1668 and 1669 cm.$^{-1}$. Though small, the difference was quite definite and it was confirmed on model compounds (Table 3). Two further cases were located in the literature (Couvreuir and Bruylants, *Bull. Soc. chim. Belg.*, 1950, **59**, 436; G. S. Myers, *J. Amer. Chem. Soc.*, 1951, **73**, 2100). As can be seen from the table the shift only applies to the double bonds in conjugation with the carbonyl—at the cell thicknesses used (~5 μ) the C=C str. frequency was not detected at all in the case of *cis*- and *trans*-

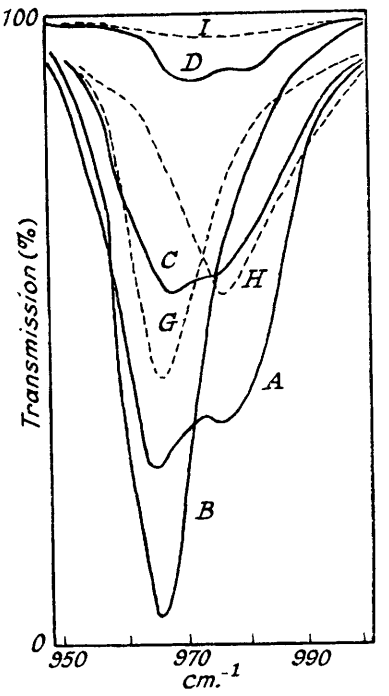



FIG. 2. *Unsaturated* C–H *deformation frequencies.*
(Detail from Fig. 1. *G*—*I* are for liquid films at qualitatively comparable thicknesses.)

*A*, *N-iso*-Butylundeca-*trans*-1 : *trans*-7-diene-1-carboxyamide.
*B*, ,, *cis*-1 : *trans*-7- ,, ,,
*C*, ,, *trans*-1 : *cis*-7- ,, ,,
*D*, ,, *cis*-1 : *cis*-7- ,, ,,
*G*, *trans*-*n*-non-4-en-1-ol.
*H*, *trans*-*N-iso*Butylundeca-1-ene-1-carboxyamide.
*I*, *cis*- ,, ,, ,,

hept-4-en-1-oic acids or in *trans*-non-5-en-1-ol. The reason is that the change in dipole moment during the C=C stretching vibration is small when the double bond is seated well within the carbon chain, but considerable when it is at the end of a chain or when a polar substituent is attached close by. Since the intensity of infra-red absorption is proportional (classically) to the square of the dipole moment change, the vibration is weak or not detectable in appropriate cases (Rasmussen, Brattain, and Zucco, *J. Chem. Phys.*, 1947, **15**, 135; Kletz and Sumner, *J.*, 1948, 1456; cf. Wotiz and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 3441). A frequency difference of the above type has long been recognised in the Raman spectra of geometrical isomers (Bourguel and Gredy, *Compt. rend.*, 1932, **195**, 129; Gredy and Piaux, *ibid.*, 1934, 198, 1235; Gredy, *Bull. Soc. chim.*, 1935, **2**, 1029; 1936, **3**, 1093, 1101; 1937, **4**, 415; *Compt. rend.*, 1936, **202**, 322; Goethals, *Bull. Soc. chim. Belg.*, 1937, **46**, 409; Ruzicka, Schinz, and Susz, *Helv. Chim. Acta*, 1944, **27**, 1561). In

* In support of this view *N-iso*butylnona-*trans*-1 : *cis*-5-diene-1-carboxyamide shows only one clean absorption at 978 cm.$^{-1}$. In this series, however, the two bands in the *trans*-1 : *trans*-5-isomer were not resolved although the shape of the absorption gives indication of their presence (Crombie, unpublished).

this case, however, the strength of the absorption depends on the polarisibility instead of on the dipole moment, and even double bonds in the interior of long carbon chains have strong Raman lines.

In view of the above evidence that the structures assigned by synthesis to the four stereoisomeric *N-iso*butylundeca-1 : 7-dienamides are correct (within the reservations mentioned regarding contamination with stereoisomers), their relation to natural herculin can now be considered. Jacobson (*J. Amer. Chem. Soc.*, 1948, **70**, 4234) records m. p. 59—60° for the natural material, so that on this basis only the *trans* : *trans*-synthetic compound might be identical though its m. p. is too low (53—54°). Furthermore, beyond a little yellowing, none of the synthetic *iso*butylamides deteriorated visibly on storage for months at room temperature whereas herculin is described as changing to a dark resin overnight. Their taste, although bitter and unpleasant, had none of the intensity and character of those natural *iso*butylamides which the present author has examined. Finally, when tested in acetone solution against adult *Tenebrio molitor* at concentrations of 1—2% all four geometrical isomers caused a mortality of less than 3%. Natural pellitorine which was described by Jacobson (*loc. cit.*) as being less toxic than herculin to houseflies caused a kill of 47% under the same conditions (actual concentration 1·17%).

Thus both chemical and physiological evidence indicate that herculin is not a stereoisomer of *N-iso*butylundeca-1 : 7-diene-1-carboxyamide. Since an original specimen of herculin was not available for direct comparison its re-isolation was undertaken. A procedure very similar to that described by Jacobson was followed. In the early stages of the isolation asarinin (xanthoxylum S) was obtained as colourless needles, m. p. 121° ($\lambda_{max.}$ 236, 286 mμ; $\varepsilon_{max.}$ 9600, 9600). The presence of this in southern prickly ash bark is well established (Colton, *Amer. J. Pharm.*, 1890, 191; Gordin, *J. Amer. Chem. Soc.*, 1906, **28**, 1649; Dieterle and Schwengler, *Arch. Pharm.*, 1939, **277**, 33; Jacobson, *loc. cit.*). At a later stage *N*-2-*p*-methoxyphenylethyl-*N*-methylcinnamamide, m. p. 75° ($\lambda_{max.}$ 223, 280 mμ; $\varepsilon_{max.}$ 21,500, 22,700), was isolated. This was first obtained from the bark by LaForge and Barthel (*J. Org. Chem.*, 1944, **9**, 250). Although asarinin is a pyrethrum synergist neither of the above compounds is insecticidally potent alone.

Finally, out of the fraction from which Jacobson isolated herculin a highly unstable unsaturated secondary amide (infra-red spectrum, Fig. 1), m. p. 63—65°, was isolated. It was markedly different from the stereoisomeric *N-iso*butylundeca-1 : 7-diene-1-carboxyamides described above and possessed the characteristic burning taste. The natural amide was highly potent when tested against houseflies (see Experimental) and a preliminary examination has shown it to be more highly unsaturated than is the diethenoid structure assigned to herculin by the American author. It has the typical ultra-violet light absorption of a conjugated triethenoid compound ($\lambda_{max.}$ 258, 270, 280 mμ, $E^{1\%}_{1\,cm.}$ 1290, 1680, 1490; O'Connor, Heinzelmann, Freeman, and Pack, *Ind. Eng. Chem. Anal.*, 1945, **17**, 467, give for elaeostearic acid: $\lambda_{max.}$ 260, 270, 281 mμ, $E^{1\%}_{1\,cm.}$ 1290, 1700, 1300, in *iso*octane). This polyeneamide is therefore named *neo*herculin and will be examined further. The nature of the herculin isolated by Jacobson must remain open.

## Experimental

The ultra-violet light absorption data (in pure ethanol) were obtained by Mrs. I. Boston, using a Hilger medium quartz instrument. Analytical data, including microhydrogenations which were determined in acetic acid with a platinum catalyst, are by Mr. Oliver of Imperial College.

The infra-red spectra were determined by the author using a Grubb–Parsons single beam spectrometer with rock-salt optics, a mechanical slit drive, and a Brown recorder. Subtraction of the atmospheric absorption on a point-to-point basis gave the curves illustrated. The error in reading the frequencies is believed to be ±15, ±2, and ±0·5 cm. at 3600, 1300, and 750 cm. respectively. Slit widths at 3850, 1300, and 750 cm. were 0·036, 0·20, and 0·88 mm. respectively. In the case of the model compounds (Table 3) only the regions of immediate interest were examined. The author is grateful to Dr. W. C. Price for the facilities afforded him in this phase of the investigation.

trans-n-*Oct*-4-*enyl Bromide*.—Phosphorus tribromide (117 g.) was added during 3 hours to a

stirred mixture of *trans*-oct-4-en-1-ol (150 g.; Crombie and Harper, *J.*, 1950, 1077) and dry pyridine (24 ml.), cooled in ice. The crude bromide was isolated by distillation at 150 mm., diluted with light petroleum (b. p. 40—60°), and washed with water, dilute hydrochloric acid (10%), and sodium hydroxide solution (10%). The petroleum layer was dried ($Na_2SO_4$) and evaporated and the residue distilled, to give trans-n-*oct*-4-*enyl bromide* (156 g., 70%), b. p. 78°/15·5 mm., $n_D^{20}$ 1·4682 (Found: C, 50·55; H, 7·85; Br, 41·3. $C_8H_{15}Br$ requires C, 50·3; H, 7·9; Br, 41·8%).

trans-n-*Oct*-4-*ene*-1-*carboxylic Acid* (V).—A Grignard reagent was prepared from *trans*-n-oct-4-enyl bromide (100 g.) and magnesium turnings (12·7 g.) in anhydrous ether (400 ml.). Dry gaseous carbon dioxide was circulated above the vigorously stirred solution until the mixture became very viscous. A large excess of crushed solid carbon dioxide was then stirred into the paste (by hand), and the mixture set aside overnight. The product was decomposed with water and dilute hydrochloric acid and extracted with ether. The ethereal extract was itself thoroughly extracted with dilute sodium hydroxide solution, and the latter washed with more ether. The purified acid was liberated by acidification (hydrochloric acid) to Congo-red and collected with ether. Working up in the usual way and distillation gave trans-n-*oct*-4-*ene*-1-*carboxylic acid* (59·2 g., 73%), b. p. 138—140°/15·5 mm., $n_D^{20}$ 1·4460 (Found: 69·3; H, 10·65. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%). The S-*benzylthiuronium* salt formed shining plates (from ethyl acetate), m. p. 145—146° (Found: C, 63·0; H, 7·95; N, 8·55. $C_{17}H_{26}O_2N_2S$ requires C, 63·3; H, 8·15; N, 8·7%).

trans-n-*Non*-5-*en*-1-*ol* (VI).—*trans*-*n*-Oct-4-ene-1-carboxylic acid (22·4 g.) in dry (calcium hydride) ether (100 c.c.) was added slowly (1 hour) to a solution of lithium aluminium hydride (5·2 g.) in dry ether (150 ml.). The ether refluxed gently. When addition was complete stirring was continued for 1 hour and the mixture decomposed with water and then dilute hydrochloric acid. Drying ($Na_2SO_4$), evaporation, and distillation yielded trans-n-*non*-5-*en*-1-*ol* (20·4 g., 93%), b. p. 107°/17·5 mm., $n_D^{20}$ 1·4475 (Found: C, 75·7; H, 12·5. $C_9H_{18}O$ requires C, 76·0; H, 12·75%). The p-*diphenylurethane* formed long colourless needles, m. p. 102°, from light petroleum (b. p. 60—80°) (Found: C, 78·65; H, 8·3. $C_{22}H_{27}O_2N$ requires C, 78·3; H, 8·05%).

The infra-red spectrum showed strong absorption at 966·5 cm.$^{-1}$, confirming the presence of a *trans*-double bond.

trans-n-*Non*-5-*enyl Bromide*.—A mixture of *trans*-*n*-non-5-en-1-ol (34 g.) and pyridine (6 ml.), when treated as above with phosphorus tribromide (24 g.), yielded trans-n-*non*-5-*enyl bromide* (40·5 g., 82·5%), b. p. 143—146°/90 mm., $n_D^{20}$ 1·4690 (Found: Br, 38·4. $C_9H_{17}Br$ requires Br, 38·95%).

trans-n-*Dec*-6-*enal* (VII).—A Grignard reagent was prepared from *trans*-*n*-nonenyl bromide (15 g.) and magnesium turnings (1·9 g.) in dry ether (25 ml.) and heated under reflux for 1 hour and then cooled to 20°. Ethyl orthoformate (11 g.) was added and the mixture refluxed for 16 hours (solid began to separate after ~15 minutes). The ether was removed by distillation and the residue decomposed with dilute hydrochloric acid (150 ml.; 4%). The aldehyde was removed by distillation in steam and isolated from the distillate (230 ml.) as its bisulphite compound (colourless plates). Addition of the latter to an excess of dilute sodium hydrogen carbonate solution, steam-distillation, and extraction with ether gave the pure aldehyde. The ethereal solution was dried, the solvent evaporated (this caused some difficulty as a stable froth formed), and the residue twice distilled, to yield *trans*-*n*-dec-6-enal (3·7 g., 38%), b. p. 117°/50 mm., $n_D^{20}$ 1·4409. Only a poor analysis was obtained (Found: C, 76·3; H, 11·6. Calc. for $C_{10}H_{18}O$: C, 77·85; H, 11·75%). The aldehyde had a characteristic odour, quite pleasant in bulk but powerful on dilution, and opinions as to its pleasantness or unpleasantness in this state varied. It formed a 2 : 4-*dinitrophenylhydrazone* which crystallised from hot ethanol first as golden-yellow flat needles, but these were followed on further cooling by red prisms. By careful crystallisations from methanol the yellow needles were isolated; they had m. p. 93° (Found: C, 57·1; H, 6·6; N, 17·5. $C_{16}H_{22}O_4N_4$ requires C, 57·4; H, 6·6; N, 16·85%).

n-*Undeca*-trans-1 : trans-7-*diene*-1-*carboxylic Acid* (VIII).—*trans*-*n*-Dec-6-enal (2·4 g.) was added slowly to a mixture of malonic acid (1·66 g.) and pyridine (1·7 ml.) and set aside in a closed vessel with a capillary leak, with occasional shaking ($CO_2$ evolved) for 5 days. All the solid had then disappeared and the product was warmed for 2 hours on the steam-bath. To the cooled liquid excess of dilute hydrochloric acid was added and the neutral plus acid material extracted with ether. The acid was purified by extraction and by liberation from 10% sodium hydroxide solution in the usual way. It was collected with ether, and the solution dried ($Na_2SO_4$), evaporated, and distilled. The n-*undeca*-trans-1 : trans-7-*diene*-1-*carboxylic acid*

(1·38 g., 45%), b. p. 140°/0·8 mm., $n_D^{20}$ 1·4737, crystallised in large colourless plates. The crystals melted at 34—35° to a turbid liquid which cleared at 36° (Found: C, 73·7; H, 10·2. $C_{12}H_{20}O_2$ requires C, 73·45; H. 10·3%). Microhydrogenation: 2·04 $H_2$. The acid had a mild odour. Its S-*benzylthiuronium salt* crystallised in shining plates (from ethyl acetate), m. p. 159° (Found: N, 7·45. $C_{10}H_{30}O_2N_2S$ requires N, 7·75%). A specimen of the acid (96 mg.) was hydrogenated in ethyl acetate in presence of palladium on calcium carbonate until no more gas was absorbed. Filtration and evaporation yielded lauric acid, m. p. 41° alone and on admixture with a specimen, m. p. 41°. Its *p*-bromophenacyl ester melted at 74·5° (lit., 76°).

N-iso*Butyl*-n-*undeca*-trans-1 : trans-7-*diene*-1-*carboxyamide* (I).—Thionyl chloride (0·3 ml.) was added to the *trans* : *trans*-acid prepared as above (554 mg.), set aside for 12 hours, and then heated at 100° for 30 minutes. The crude acid chloride was diluted with benzene (5 ml.), and excess of *iso*butylamine (0·7 ml.) added dropwise with cooling to moderate the vigorous reaction. The product was set aside for 30 minutes and then washed with 10% hydrochloric acid, 10% aqueous sodium hydroxide, and water. The benzene solution was dried and evaporated, and the residue distilled, having b. p. 145°/4 × $10^{-3}$ (600 mg.); it rapidly crystallised to a straw-yellow mass of needles, m. p. 46—47°, clear at 51°. The material proved difficult to crystallise but colourless needles, obtained from light petroleum (b. p. 40—60°), had m. p. 53—54°. For analytical and other purposes the solution in light petroleum was treated with charcoal and kieselguhr and filtered and the filtrate evaporated. The residue (faintly yellow only) was dried at 70°/0·2 mm. for 3 hours to remove all traces of solvent and melted at 53°, clear at 54·5° (Found: C, 76·05; H, 11·75; N, 5·25. $C_{16}H_{29}ON$ requires C, 76·45; H, 11·65; N, 5·5%). Microhydrogenation: 1·95 $H_2$. For the light absorption see Table 2.

trans-n-*Undeca*-7-*en*-1-*yne* (IX).—Sodamide was prepared in liquid ammonia (200 ml.) from sodium (2·5 g.) and a ferric nitrate catalyst. Scrubbed ($H_2SO_4$) acetylene was passed in to form sodium acetylide in the usual way and *trans-n*-non-5-enyl bromide (15 g.) added in ether (10 ml.). The flask was lagged and the mixture was stirred for 18 hours. Excess of ammonium chloride was then added and the ammonia evaporated off on a steam-bath. The residue was treated with dilute sulphuric acid, and the acetylenic hydrocarbon isolated by ether-extraction. This solution was worked up in the usual way to give, after two distillations, trans-n-*undeca*-7-*en*-1-*yne* (6·8 g., 62%), b. p. 82—84°/18 mm., $n_D^{20}$ 1·4462 (Found: C, 88·1; H, 12·1. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%). Although it gave an immediate white precipitate with alcoholic silver nitrate, yet when treated with Johnson and McEwen's potassiomercuric iodide reagent (*J. Amer. Chem. Soc.*, 1926, **48**, 469) only a white turbidity was obtained which after a few minutes became a turbid green, a small amount of crystalline material separating.

trans-n-*Undeca*-7-*en*-1-*yne*-1-*carboxylic Acid* (X).—Ethylmagnesium bromide was prepared in dry ether (100 c.c.) from magnesium (1·5 g.) and ethyl bromide (6·8 g.). *trans-n*-Undeca-7-en-1-yne (6·0 g.) in ether (20 c.c.) was added slowly and the mixture refluxed for 3 hours. The acetylenic Grignard solution was then poured carefully on a large excess of crushed solid carbon dioxide and set aside overnight. An excess of dilute hydrochloric acid was added and the ethereal phase separated. The acid was extracted with dilute sodium hydroxide solution and purified and worked up in the usual way. Distillation gave pure trans-n-*undeca*-7-*en*-1-*yne*-1-*carboxylic acid* (3·4 g., 44%), b. p. 125—126°/0·04 mm., $n_D^{20}$ 1·4745 (Found: C, 74·55; H, 9·7. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·35%). Microhydrogenation: 2·96 $H_2$. The S-*benzylthiuronium* salt of the acid crystallised in needles (from ethyl acetate), m. p. 180° (Found: N, 7·45. $C_{20}H_{28}O_2N_2S$ requires N, 7·75%).

n-*Undeca*-cis-1 : trans-7-*diene*-1-*carboxylic Acid* (IX).—*trans-n*-Undeca-7-en-1-yne-1-carboxylic acid (1·93 g.) was hydrogenated in methyl acetate (15 ml.) with pre-reduced palladium on calcium carbonate (5%; 150 mg.) until hydrogen equivalent to one mol. (224 ml. at N.T.P.) had been absorbed. Kieselguhr was added and the catalyst filtered off. The solvent was evaporated and the residue distilled, to give n-*undeca*-cis-1 : trans-7-*diene*-1-*carboxylic acid* (1·35 g.), b. p. 115—117°/0·5 mm., $n_D^{20}$ 1·4682—1·4693. Microhydrogenation: 1·80 $H_2$. The acid was refractionated and then had b. p. 127—129°/1·0—1·1 mm., $n_D^{20}$ 1·4692—1·4699 (Found: C, 73·15; H, 10·5. $C_{12}H_{20}O_2$ requires C, 73·45; H, 10·3%). Microhydrogenation: 1·80 $H_2$. Its S-*benzylthiuronium* salt (Found: N, 7·55%) when crystallised from ethyl acetate formed shining plates, m. p. 148°. The derivative melted quite sharply, but repeated re-determinations showed that, for this and certain other *S*-benzylthiuronium salts mentioned, the value obtained was not always precisely repeatable: variations of a few degrees on either side of the m. p. quoted were obtained. Other derivatives would seem preferable for characterisation but these salts were used in order to effect a comparison with the isomers recorded in the literature.

The *cis*-1 : *trans*-7-acid (101 mg.) was hydrogenated, as described for the *trans*-1 : *trans*-7-acid and yielded lauric acid, m. p. 41° alone and on admixture with a commercial specimen.

trans-N-iso*Butyl*-n-*undeca*-7-*en*-1-*yne*-1-*carboxyamide* (XII).—The acetylenic acid (522 mg.) was converted into the acid chloride with thionyl chloride (0·3 ml.) during 2 hours at 20° and 1 hour at 60°. This was diluted dry benzene (5 ml.), and excess of *iso*butylamine added to the chilled solution. Working up as described for the *iso*butylamide above gave trans-N-iso*butyl*-n-*undeca*-7-*en*-1-*yne*-1-*carboxyamide* (509 mg.), b. p. 159—160°/0·2 mm., $n_D^{20}$ 1·4854 (Found: N, 5·4. $C_{16}H_{27}ON$ requires N, 5·6%).

N-iso*Butyl*-n-*undeca*-cis-1 : trans-7-*diene*-1-*carboxyamide*.—(*a*) *trans*-*N*-*iso*Butyl-*n*-undeca-7-en-1-yne-1-carboxyamide (409 mg.) was hydrogenated in ethyl acetate (8 ml.) with pre-reduced palladium on calcium carbonate (5%; 100 mg.). After semihydrogenation (36·8 ml. at N.T.P.), the *iso*butylamide was isolated in the usual way. Distillation yielded N-iso*butyl*-n-*undeca*-cis-1 : trans-7-*diene*-1-*carboxyamide*, b. p. 154°/0·6 mm., 142°/3 × $10^{-2}$ mm., $n_D^{20}$ 1·4824. Microhydrogenation: 1·91 $H_2$.

(*b*) The *cis*-1 : *trans*-7-acid (0·585 g.) was refluxed with oxalyl chloride (1·0 ml.) in anhydrous benzene (5 ml.) for 1 hour and the solvent and excess of reagent were removed *in vacuo* at 20°. Ether (20 ml.) and excess of *iso*butylamine (1·0 ml.) were added and the mixture was set aside for 1 hour. Water was added, and the ethereal layer separated and worked up as described for the *trans*-1 : *trans*-7-isomer. Distillation gave *N*-*iso*butyl-*n*-undeca-*cis*-1 : *trans*-7-diene-1-carboxyamide, b. p. 128—130°/4 × $10^{-3}$ mm., $n_D^{15}$ 1·4795 (Found: C, 76·4; H, 11·95; N, 5·25%). Microhydrogenation: 1·88 $H_2$.

*Non*-1-*yne*.—*n*-Heptyl bromide (25·7 g.) was added to sodium acetylide (prepared from sodium, 4·0 g., with an iron catalyst for the formation of sodamide) in liquid ammonia (300 ml.) and stirred overnight. The ammonia was evaporated off, water and ether were added, and the nonyne (9·7 g., 53%) was isolated in the usual way; it had b. p. 149—152°, $n_D^{21}$ 1·4261 (Bourguel, *Ann. Chim.*, 1925, **3**, 359, gives b. p. 149°, $n_D^{20}$ 1·423, and Truchet, *ibid.*, 1931, **16**, 410, gives b. p. 149—151°, $n_D^{20}$ 1·426, for specimens prepared by the isomerisation of non-2-yne).

*Non*-1-*yne*-1-*carboxylic Acid*.—A Grignard reagent was prepared from ethyl bromide (8·2 g.) and magnesium (1·8 g.) in ether. Non-1-yne (6·2 g.) was added and the mixture refluxed for 6 hours, poured on a large excess of solid carbon dioxide, and sealed for 36 hours in an autoclave. The product was decomposed with dilute hydrochloric acid, and the acid extracted with ether and separated from neutral products by dilute aqueous sodium hydroxide. Liberation of the acetylenic acid with a slight excess of dilute hydrochloric acid (Congo-red), extraction with ether, and distillation furnished non-1-yne-1-carboxylic acid (4·2 g., 50%), b. p. 110—111°/0·3 mm., $n_D^{18}$ 1·4617 (Found: C, 71·0; H, 9·55. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·6%) (Moureu and Delange, *Compt. rend.*, 1903, **136**, 554, *Bull. Soc. chim.*, 1903, **29**, 660, give b. p. 164—168°/18—20 mm.).

N-iso*Butyl*-n-*non*-1-*yne*-1-*carboxyamide*.—Thionyl chloride (1·3 g.) was added to non-1-yne-1-carboxylic acid (1·3 g.) and set aside overnight. After 30 minutes' refluxing the crude acid chloride was diluted with ether and cooled in ice, and *iso*butylamine (3 ml.) in ether (10 ml. was added dropwise. After washing with acid and alkali and distillation, the required acetylenic iso*butylamide* (1·48 g., 82%), b. p. 130—132°/5 × $10^{-4}$ mm., $n_D^{17}$ 1·4752, was isolated (Found: N, 5·7. $C_{14}H_{25}ON$ requires N, 6·25%).

N-iso*Butyl*-cis-n-*non*-1-*ene*-1-*carboxyamide*.—The acetylenic *iso*butylamide (0·974 g.) was hydrogenated in ethyl acetate (5 ml.) with pre-reduced palladium (5%) on calcium carbonate until 90 c.c. of hydrogen at 20°/758 mm. (1 mol., 105 ml.) had been absorbed. The catalyst was filtered off and the solution evaporated and distilled, one fraction, b. p. 121°/2 × $10^{-4}$ mm., $n_D^{21}$ 1·4704 (0·752 g.), being collected. This was redistilled and the middle fraction b. p. 128°/9 × $10^4$ mm., $n_D^{23}$ 1·4689, used for spectroscopic work and for analysis (Found: N, 5·8. $C_{14}H_{27}ON$ requires N, 6·2%). Microhydrogenation: 1·08 $H_2$.

trans-n-*Non*-1-*ene*-1-*carboxylic Acid*.—*n*-Octaldehyde (9·6 g.; b. p. 172—175, $n_D^{22}$ 1·4170) was added to a cooled mixture of pyridine (8 ml.) and malonic acid (7·8 g.) and set aside at room temperature until all solid had disappeared (3 days with occasional shaking). It was then heated on a steam-bath for 2 hours, diluted with water, and acidified, and the acidic and neutral materials were isolated with ether. The acid was purified by extraction with aqueous sodium hydroxide (10%) and isolated in the usual way. Distillation gave *trans*-non-1-ene-1-carboxylic acid (6·5 g., 51%), b. p. 113—114°/0·3 mm., $n_D^{15}$ 1·4630 (Found: C, 70·05; H, 10·65. $C_{10}H_{18}O_2$ requires C, 70·55; H, 10·65%). Zaar (*Ber. Schimmel and Co., A.-G.*, 1929, 299; *Chem. Abs.*, 1930, **24**, 2107) gives b. p. 148—149°/4·5 mm., $n_D^{20}$ 1·4616.

N-iso*Butyl*-trans-n-*non*-1-*ene*-1-*carboxyamide*.—The *trans*-acid (1·87 g.) when converted into

the crude acid chloride with thionyl chloride and added to an excess of *iso*butylamine afforded the required N-iso*butylamide* (2·07 g.), b. p. 140°/8 × $10^{-4}$ mm., which rapidly solidified to waxy needles, m. p. 48—49° (Found: C, 74·5; H, 12·3; N, 5·85. $C_{14}H_{27}ON$ requires C, 74·6; H, 12·1; N, 6·2%). Microhydrogenation: 0·98 $H_2$.

N-iso*Butyl*-trans-*prop*-1-*ene*-1-*carboxyamide* (Crotono*iso*butylamide).—Prepared in the usual way this formed sheaves of needles, m. p. 71°, from light petroleum (b. p. 40—60°) (Found: C, 67·55; H, 10·2. Calc. for $C_8H_{15}ON$: C, 68·05; H, 10·7; N, 9·9%).

*Examination of Southern Prickly Ash Bark.*—The bark was a gift from Messrs. S. B. Penick, New York, which was received through the good offices of Dr. S. H. Harper. Ground bark (5 kg.) was macerated under nitrogen with light petroleum (b. p. 40—60°) for 12 days and the extract syphoned off. It was then macerated with four further portions (5 l. each) of light petroleum and the united extracts were evaporated to 2·5 l. This solution was successively extracted with one portion of 280 ml., three of 225 ml., and two of 100 ml. of nitromethane. The nitromethane was removed *in vacuo* and the residue dissolved in ether (400 ml.) and washed with hydrochloric acid (10%), sodium hydroxide solution (10%), and water. The aqueous alkali tended to form emulsions.

When the purified ethereal solution was set aside at 0° for 24 hours solid was deposited which crystallised from ethanol as long colourless needles, m. p. 121°, $[\alpha]_D^{21}$ −125° (*c*, 2·90%, chloroform) (Found: C, 67·9; H, 5·35. Calc. for $C_{20}H_{18}O_6$: C, 67·8; H, 5·1%). Huang-Minlon (*Ber.*, 1937, **70**, 951) gives m. p. 121—122°, $[\alpha]_D^{18}$ −122° (*c*, 3·54%, chloroform), for asarinin. For the ultra-violet light absorption, see p. 3000. G. Aulin Erdtmann and H. Erdtmann (*Svensk Papperstidn.*, 1944, **47**, 22) record $\lambda_{max.}$ 237, 287 mμ; $\varepsilon_{max.}$ 9300, 8300. The green-brown solution was evaporated *in vacuo* and the residue extracted with boiling light petroleum (b. p. 60—80°; 10 × 100 ml.). A brown syrup remained undissolved, and oil separated from the hot solutions which were concentrated to 400 ml. and then decanted; the solution was set aside at 0° for 36 hours. Crystals (1·4 g.), m. p. 58—72°, were deposited. After four recrystallisations from light petroleum (b. p. 40—60°) the material (colourless needles) melted at 75°. For ultra-violet light absorption, see p. 3000. LaForge and Barthel (*loc. cit.*) give m. p. 76° for *N*-2-*p*-methoxyphenylethyl-*N*-methylcinnamamide.

Further concentration of the main solution to 120 c.c. and chilling at 0° for 36 hours caused no more crystallisation, so the solution was cooled to −50° for 30 minutes. A gel (A) separated which was filtered off. The filtrate was further concentrated and set aside at 0° for 3 weeks but only a small amount of crystallisation was induced. Finally, it was evaporated *in vauco* and used for insecticidal tests as below. Recrystallisation of (A) (which formed an amorphous pad on filtration) from light petroleum (b. p. 60—80°) with charcoal and kieselguhr and cooling to 0° gave crude neo*herculin*, m. p. 57—58° (2·0 g.). A portion was twice recrystallised as above, washed with cold light petroleum (b. p. 40—60°), and dried at 0·05 mm. It formed colourless needles, m. p. 63—65° (Found: N, 5·25. $C_{16}H_{25}ON$ requires N, 5·65%). Jacobson (*loc. cit.*) gives m. p. 59—60° for herculin. The hydrogenation number was 65·7. For ultra-violet light absorption, see p. 3000. Although unstable at room temperature (and, though less so, at 0°) in the presence of air, a specimen sealed *in vacuo* has been preserved at 0° for more than a year without deterioration.

*neo*Herculin in odourless petroleum distillate containing 15% of *cyclo*hexanone was tested against houseflies by Dr. E. A. Parkin of the Pest Infestation Laboratory (D.S.I.R.), Slough. It was 4·2 times as toxic as the oily mother-liquors (see above) and the concentration equivalent to a 0·1% (w/v) solution of standard natural pyrethrins was between 0·13 and 0·18% (24 hours' mortality count). Although showing some knock-down effect (10 minutes), neither of the samples was as good as 0·1% pyrethrins, even at 1·0% strength.

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