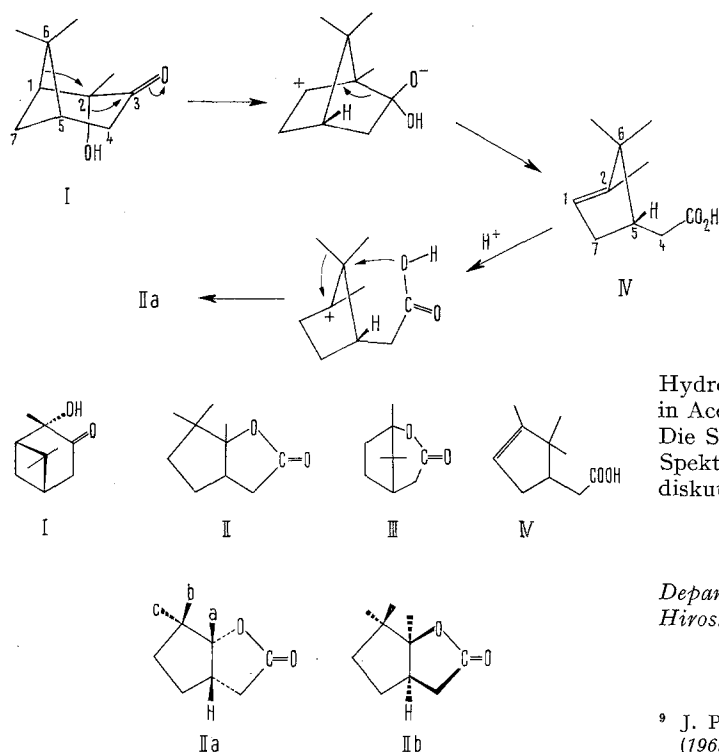


rule⁹, IIa should exhibit a negative and IIb a positive Cotton effect. The ORD and CD curves were then found to exhibit the negative Cotton effect: $[\phi]_{225}^{\text{shoulder}} - 1550^{\circ}$ (in MeOH); $[\theta]_{210}^{\text{max}} - 328^{\circ}$ (in MeOH). The stereochemistry of (-)-dihydro- β -campholenolactone (II) was consequently clarified to be IIa.

In order to clarify the mechanism of formation of lactone II from the hydroxy-ketone I, the acetone solution of I was treated with anhydrous oxalic acid during a shorter reaction time in the same manner as above. The formation of (-)- α -campholenic acid (IV) expected



as an intermediate was proven by isolation from the reaction mixture in 6% yield. On the other hand, treatment of (+)- α -campholenic acid (IV) with anhydrous oxalic acid under the same conditions was found to yield (+)- γ -lactone II (41%) and (-)-1,2-campholide (III) (22%). α -Campholenic acid (IV) was thus evidenced as an intermediate product to produce γ -lactone II from hydroxy-ketone I.

The formation of dihydro- β -campholenolactone (II) is best explained as involving the Wagner-Meerwein type rearrangement of I to the intermediate IV, which then undergoes protonation at an ethylenic bond, 1,2-shift of a methyl group, and lactonization to yield II, as shown in the Scheme. On the other hand, the formation of 1,2-campholide (III) from α -campholenic acid is interpreted as undergoing lactonization between the carboxyl group and the C-2 carbon of the carbonium ion. These reactions support the supposition that the C-2 methyl group of 2-hydroxypinocampone (I) is *cis* with respect to the gem-dimethyl bridge, as discussed recently in our paper².

Zusammenfassung. Die Reaktion von (-)-2-Hydroxypinocampone (I) mit wasserfreier Oxalsäure in Aceton liefert (-)-Dihydro- β -campholenolacton (IIa). Die Stereochemie liess sich durch NMR-, ORD- und CD-Spektren bestimmen. Es wird ein Reaktionsmechanismus diskutiert.

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Hiroshima University, Hiroshima (Japan), 17 April 1970.

⁹ J. P. JENNINGS, W. KLYNE and P. M. SCOPES, J. chem. Soc. (1965), 7211.

Identification of Odorous Compounds from Male Lepidoptera

Males of many species of Lepidoptera emit odorous compounds from specialized scales, 'hair pencils' or brush-organs. Males of the nocturnal moth, *Phlogophora meticulosa* (L.) release scent to induce the female to copulate¹ and about $\frac{1}{3}$ of the 300 British Noctuidae have similar brushes to those described from *P. meticulosa*², consisting of paired abdominal glands, brushes and storage pockets. The brushes store and disperse scent synthesized in glands remote from them so that only the final secretion product occurs on the brushes.

Method. Each brush was cut across its base while still in the pocket, carefully removed so that very little scent was lost, and extracted in carbon tetrachloride. Solutions were analyzed in the first instance by gas chromatography and the components identified using combined gas-liquid chromatography (GLC)-mass spectrometric methods³. All components so identified were commercially available or easily synthesized for control purposes. We thank Dr. W. H. McFADDEN (I.F.F.; USA) for comparing one of our spectra with his reference collection and for supplying a sample of pinocarvol for oxidation to pinocarvone.

Results. The identities and relative proportions of the compounds isolated from the brushes of 8 species of Noctuidae are given in the Table.

We had previously shown that benzaldehyde is the major component of the scent in 2 *Leucania* species⁴, but the minor component, iso-butyric acid, was then undetected. Males of *Bapta temerata* (Schiff.) in the family Geometridae secrete *n*-butyric acid apparently for the same function. The first two components from *P. meticulosa* which we had previously thought to be a single compound near benzaldehyde, are now found to be

¹ M. BIRCH, Anim. Behav. 18, in press (1970).

² M. BIRCH, Trans. R. ent. Soc. Lond., in press (1970).

³ Pye 104-4 GLC, with flame ionization detector, argon carrier gas and columns of 15% polyethylene glycol adipate, 5% carbowax 20M and 30% 'Apiezon L' on 80-100 mesh 'Embacil'; effluent from the GLC was led via a Bieman Watson separator into the source of an A.E.I.-MS9 mass spectrograph.

⁴ R. T. APLIN and M. C. BIRCH, Nature 217, 1167 (1968).

Components isolated from the brushes of male noctuid moths

	Component	mol. wt.	%	Component	mol. wt.	%
<i>Leucania impura</i> (Hueb.)	Benzaldehyde	106	80	Iso-butyric acid	88	20
<i>Leucania comigera</i> (Schiff.)	Benzaldehyde	106	80	Iso-butyric acid	88	20
<i>Leucania pallens</i> (L.)	Benzaldehyde	106	80	Iso-butyric acid	88	20
<i>Polia nebulosa</i> (Huf.)	Benzaldehyde	106	8	Benzyl alcohol	108	10
	2-Phenyl ethanol	126	70			
<i>Mamestra persicariae</i> (L.)	Benzaldehyde	106	10	Benzyl alcohol	108	2
	2-Phenyl ethanol	126	85			
<i>Mamestra brassicae</i> (L.)	?	166	85+			
<i>Phlogophora meticulosa</i> (L.)	6-Methyl-hept-5-en-2-one	126	63			
	6-Methyl-hept-5-en-2-ol	128	28			
	2-Methyl butanoic acid	128	9			
<i>Apamea monoglypha</i> (Huf.)	Pinocarvone	150	95			

6-methyl-hept-5-en-2-one and the corresponding alcohol. The equivalent of 1 µg per brush of 6-methyl-hept-5-en-2-one was extracted from a sample of 300 brushes of *P. meticulosa*. The total quantity produced by one moth will certainly be much greater since moths trapped in the field would probably have mated at least once before capture, everting the brushes and losing a high proportion of scent. Losses also occur through chemical change (e.g. benzaldehyde to benzoic acid).

The male scents have been identified without reference to their biological function. The apparently identical nature of the scent of 3 *Leucania* species would suggest that at least between these species the male scents are not acting to promote species isolation. We do not know whether females can or do distinguish between the slight differences in the male scents of *M. persicariae* and *Polia nebulosa*. Both are very closely related. In contrast, the divergence between the scents of the undoubtedly congeneric *Mamestra* species suggests that in this genus the male scent may have been instrumental in speciation. Pinocarvone, found in *A. monoglypha*, has not previously been isolated from insects, though pinenes, derived from their host trees are used by bark beetles (Coleoptera) as sex pheromones and in aggregation⁵.

It seems likely that the scents will have the same function in all Noctuidae since the brush-organs are morphologically virtually identical in the family. Chemical composition of the scents agrees with sub-family divisions. Both species of Amphipyridae (*P. meticulosa* and *A. monoglypha*) secrete terpenes, the 5 species of Hadeninae secrete aromatic compounds. This correlation is being extended as material becomes available⁶.

Zusammenfassung. Die flüchtigen Anteile aus den männlichen Duftorganen von 7 Gattungen der Noctuiden wurden gaschromatographisch identifiziert.

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University of Oxford, Dyson Perrins Laboratory, Oxford OX1 3 QY (England), 14 May 1970.

⁵ G. B. PITMAN, *Science* 166, 905 (1969).

⁶ This work was supported by the Science Research Council.

Effect of a Growth-Promoting Factor on Protein Synthesis and Amino Acid Transport in vitro

In a recent paper we reported on a growth-promoting factor obtained from an extract of calf muscle. Gel filtration of the extract on a Sephadex G-25 column indicated that the active substances in the extract were polypeptides¹. Previously, Kostyo² had suggested that the action in vitro of growth hormone on protein synthesis and on amino acid transport into the diaphragms of hypophysectomized rats is mediated by a protein or polypeptide; this protein or polypeptide, first synthesized under the influence of growth hormone, would be responsible for the later stimulation of the membrane-transport mechanism. Considering our finding and the possibility suggested by Kostyo, we have examined the effect in vitro of the growth-promoting polypeptides obtained from calf muscle on amino acid transport into the diaphragms of hypophysectomized rats, and on protein synthesis. There we used as an indicator of protein synthesis the incorpora-

tion of ¹⁴C-leucine into proteins, and as an indicator of transport the intracellular accumulation of ¹⁴C-labelled α-amino-isobutyric acid (AIB).

In our experiments, 32 female hypophysectomized rats, body weight 70–80 g, purchased from Hormone Assay Laboratories (Chicago) were used. The rats were sacrificed by decapitation and hemidiaphragms were prepared by the procedure of Kostyo and KNOBIL³. Each hemidiaphragm was incubated in 10 ml Krebs-Ringer bicarbonate buffer, pH 7.4, containing 2 mg glucose per ml.

¹ M. Božović, H. Boström, K. Uthne, K. Berntsen and L. Božović, *Experientia* 26, 156 (1970).

² Y. L. Kostyo, *Ann. N.Y. Acad. Sci.* 148, 389 (1968).

³ Y. L. Kostyo and E. Knobil, *Endocrinology* 65, 525 (1959).