さらに，省力的な駆除法では，DDVP 樹脂蒸散剤がその目的を達し得ることが明らかになった．この殺虫力については第6表の結果で明らかな如く，6 m³ に1枚の使用量で高い殺虫力が認められた．また，アカイエカに対しても効果があり，薬剤感受性はアカイエカ＞イエバエ＞オオチョウバエの順に低下することを知った．

LD_{50} 値についてみれば第7表に記載された如く，Baytex>DDVP>Sumithion>pyrethrins>Phthalthrin >Malathion > Diazinon > γ-BHC > Allethrin の順に殺虫力の低下する傾向にあることがわかった．

LD_{50} 値と実用製剤の効力順位とはかならずしも平行関係にはないが，オオチョウバエ成虫の駆除には DDVP が最も適切なる殺虫剤と考えられた．

文　献

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2) 林　晃史・廿日出正美・池野直志 (1969) 防虫科学，34 (3)：115～119.

Résumé

Au cours de l'étude sur la destruction les auteurs ont observé que les insecticides de pyréthroïdes sont effectifs si l'on les pulvérise directement, tandis que DDVP ou Diazinon l'est au cas du traitement de résidus; et que le Moth Fly est moins influencé que la Mouche Domestique par ces insecticides.

Attractancy of Some Methyl Ketones Isolated from Cheddar Cheese for Cheese Mites. Takumi Yoshizawa, Izuru Yamamoto and Ryo Yamamoto (Department of Agricultural Chemistry, Tokyo University of Agriculture, Setagaya, Tokyo) Received March 4, 1970. *Botyu-Kagaku* 35, 43, 1970.

6. チェダー・チーズ中のコナダニ誘引物質

芳沢宅実，山本　出，山本　亮（東京農業大学農学部農芸化学科，東京都世田谷区）

ケナガコナダニ *Tyrophagus putrescentiae* に対するチェダー・チーズ中の主誘引因子を分離し，heptan-2-one, octan-2-one, nonan-2-one および 8-nonen-2-one であると同定した．これらの混合物は顕著な誘引性を示したが，単独では効果はなかった．

8-nonen-2-one はチーズ成分として新たに発見したもので，その合成を行ない構造を確認した．

Many kinds of food products, such as cheese, dry powdered milk, powdered grains, chocolate, spice, bean paste, and dry fish are infested with mite, causing serious losses. The cheese mite, *Tyrophagus putrescentiae*, is one of the most serious pests in Japan, and cheddar cheese is known to be one of the attractive host for it. This paper reports on the separation and characterization of main attractive substances contained in cheddar cheese.

The following approaches were necessary to solve the attractancy of cheddar cheese to the mite, since individual compound isolated from the cheese did not show any significant attractancy.

1) Removal of substances which were not responsible for the attractancy as much as possible.

2) Fractionation of crude extract into several fractions as the activity was still remained at least in one fraction.

3) Characterization of all substances in the active fraction.

4) Finding the essential combination of components for recovering the attractancy of the given fraction.

5) Elucidation of the biological relationship among fractions which were individually inactive or less active but synergistically active to other fractions.

6) Characterization of all substances contained in the fraction which showed synergistic activity by mixing with the active fraction.

Experimental

As has been reported, a sensitive bioassay method was newly devised for the isolation of the active principle. The apparatus used for this method consisted of test tubes containing samples to be tested, and mites released were trapped by olfactory response to the sample in the tubes[1].

To concentrate the attractive substances, 100 kg of cheddar cheese aged for 6 months or more was lyophilized untill all the active substances

moved to the volatile part (14 g). This volatile part was treated with 5% aqueous sodium hydroxide and 5% hydrochloric acid to give the neutral substances (4.4 g), which showed a significant attractancy even at 0.1 μg/tube. The neutral fraction was a mixture showing more than 50 peaks by gas chromatographic analyses, and the attractive substances were found to be concentrated in rather volatile fraction. It was noticeable that the acidic fraction, which was not attractive by itself, partially masked the attractancy of the neutrfral action. The attractive volatile substances (1.4 g) was obtained by sweep-codistillation of the neutral fraction at 50° to 70°C under nitrogen stream to separate from the inactive substances of low volatility. Seven hundred mg of the volatile substances were subjected to a silica gel column chromatography (50 g in 3×19 cm column), eluted successively with *n*-pentane (200 m*l*), 15% ether in pentane (100 m*l*), 20% ether in pentane (300 m*l*), 25% ether in pentane (200 m*l*), ether (100 m*l*), acetone (100 m*l*) and methanol (100 m*l*), and separated into 13 fractions. Only fractons 4, 5, and 6 eluted with 20% ether in pentane were active, though a mixture combined the fractions gave about 1/6 of the attractancy of the volatile substances before the chromatography by the bioassay.

When the fractions were subjected to a gas chromatography (2 m×3 mm i.d., 20% PEG-20M on 60 to 80 mesh chromosorb W (NAW); column temp. 90°C for 10 min., and then programmed at 2.5°C/min. to 200°C; nitrogen gas 0.6 kg/cm²), the fractions gave 6 peaks showing retention times of 5.45, 9.2, 15.2, 18.65, 24.1 and 28.0 minutes. Sodium borohydride reduction resulted in the orderly shifted to higher retention times of respective peaks, and iodoform reaction resulted in the disappearance of the original peaks. These results suggested that the peaks were methyl ketones which had been found in cheese[2]. These methyl ketones were identified as heptan-2-one (retention time 5.45), octan-2-one (9.2), nonan-2-one (15.2), undecan-2-one (24.1), and tridecan-2-one (28.0) respectively by co-gas chromatography with the authentic samples, co-gas chromatography of the sodium borohydride reduction products with the authentic secondary alcohols, and that of methyl esters of respective carboxylic acids after iodoform reaction.

It has not been known such a methyl ketone as corresponding to the retention time of 18.65 minutes. The yield of this methyl ketone was estimated to be 2 mg per 100kg of cheese. Catalytic hydrogenation with Pd-charcoal produced a peak identical with nonan-2-one. Ozonolysis of the methyl ketone gave a product, and 2,4-dinitrophenylhydrazone of it was identical with formaldehyde dinitrophenylhydrazone by thin layer chromatography. The mass spectrum showed molecular weight of 140 and the fragmentations corresponded to a methy ketone (m/e, 97, 82, 58, 43). These results suggested this methyl ketone is 8-nonen-2-one. However, the result of mass spectrum did not inform position of the double bond in the molecule. Thus, 8-nonen-2-one was synthesized from acetylene. 8-Nonyn-2-one obtained by the procedure of Barbier and Hugel[3] was partially hydrogenated with Lindlar catalyst to the desired 8-nonen-2-one. 3-Nonen-2-one (*cis*, *trans*), 7-nonen-2-one (*cis*, *trans*), 5-nonen-2-one (*trans*), 6-nonen-2-one (*cis*, *trans*) were also synthesized for the comparison. But, none of them were identical with the methyl ketone in the retention time and the mass spectrogram. The isolated methyl ketone and synthetic 8-nonen-2-one were analyzed by gas chromatography-mass spectrography (Hitachi K-53 GLC: 45 m×0.5 mm i.d., MBM column; column temp. 100°C, injection temp. 270°C; helium gas, 1 kg/cm², Hitachi RMU-6E MS; ionizing volt, 70 eV). Each sample and a mixture of both sample gave a single peak of the retention time of 21.61 minutes, and the fragmentation patterns of the mass spectrograms were identical each other.

The methyl ketones identified did not show any significant attractancy at a level of 1 μg/tube or more, but only 8-nonen-2-one showed a slight attractancy at 1 μg/tube. It was evident, however, that a mixture of heptan-2-one, octan-2-one, nonan-2-one and 8-nonen-2-one in the ratio of 5:1:1:1 was highly attractive at the level of 0.1 μg/tube. This phenomenon is considered to be "synergism". It seemed that undecan-2-one and tridecane-2-one were not involved in the attractancy. The mixture mentioned above did not

recover the attractancy shown by cheese or neutral volatile fraction. Other substances, probably alcohols and esters contained in the inactive or less active fractions may synergistically interact with the identified attractactnts.

The present experiments were the first case to elucidate the olfactory response of mites on the stored food products.

Summary

Attempts were made to isolate attractants for the cheese mite, *Tyrophagus putrescentiae*, from cheddar cheese, and heptan-2-one, octan-2-one, nonan-2-one and 8-nonen-2-one were identified as the active principles. These compounds did not show significant attractancy to the mite when applied individually, but a mixture of them showed a potent attractancy. Among them, 8-nonen-2-one was newly found from cheese by the present study.

References and Notes

1. Yamamoto, I and R. Yamamoto, reported in a seminar as a part of the United States-Japan Cooperative Science Program, held 16-18 January 1968 in Honolulu.
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3. Barbier, M. and M. F. Huegel, *Bull. Soc. Chim.* 1961, 1324.

4. This investigation was supported by a grant made by the United States Department of Agriculture under PL 480, project No. ALL-MQ-3, grant No. FG-Ja-120. We thank Takasago Perfumery Co., Ltd. and Kitasato University for taking mass spectrograms.

Insecticidal Activity of a New Synthetic Chrysanthemic Ester, 5-Propargylfurfuryl Chrysanthemate (Prothrin). Hiroshi Ogami, Yasutoshi Yoshida and Yoshio Katsuda (Research Laboratory of Dainippon Jotyugiku Co., Ltd., Osaka), Junshi Miyamoto and Tadaomi Kadota Research Department, Pesticides Division, Sumitomo Chemical Co., Ltd., Osaka) Received April 28, 1970. *Botyu-Kagaku*, 35, 45, 1970. (with English Summary 55)

7. 新合成ピレスロイド・プロスリンの殺虫特性 大神 弘，吉田安俊，勝田純郎（大日本除虫菊株式会社中央研究所）宮本純之，門田忠臣（住友化学工業株式会社農薬事業部 研究部） 45. 2. 28 受理.

新合成ピレスロイド“プロスリン”の主要衛生害虫に対する殺虫性をピレトリン，アレスリンおよびフタルスリンなどと種々の施用法により比較した．

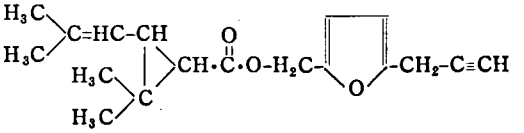
その結果プロスリンは微量滴下法ではイエバエおよびアカイエカ成虫に対して，他のピレスロイドの数倍の殺虫力を示した．特に蚊取線香など燻蒸剤としての効力は抜群で，アカイエカおよびイエバエ成虫に対し，種々の試験方法でいずれもアレスリンの 2～4 倍の効力を示した．一方プロスリンは哺乳動物に対しては極めて低毒性であった．

緒　　言

除虫菊乾花の殺虫成分ピレトリン類は，昆虫に対する速効性と，広範囲の昆虫に有効で，しかも長年にわたる使用に際しても昆虫に対する抵抗性ができず，一方温血動物に対する毒性が極めて低いことなどから安全殺虫剤として広く使用されている．

一方 LaForge ら[1]によるアレスリンの発見を契機としてピレスロイド系殺虫成分の研究開発は活発となりフタルスリン[2]，レストリン[3]などのすぐれた合成ピレスロイドが創製されるにいたった．

プロスリンは勝田ら[4]によって発見された新合成ピレスロイドで次のような構造式をもつ化合物である．



5-propargylfurfuryl (±)-*cis*, *trans*-chrysanthemate

本報では主要衛生害虫に対するプロスリンの殺虫性を種々の施用法でピレトリン，アレスリンおよびフタルスリンと比較し，同時に実用的剤型での殺虫効力の検討を行なった．

実験材料および方法

I. 供試薬剤

プロスリン：(5-propargylfurfuryl (±)-*cis*, *trans*-chrysanthemate) は bp. 120～122°C/0.20 mm Hg,