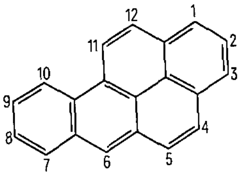
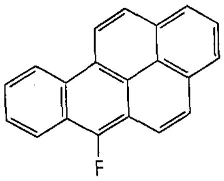
effected at −45 °C. Subsequently, the reaction mixture was kept at −78 °C for 24 h. The dark brown complex was decomposed with aqueous sodium bicarbonate. Careful column chromatography of the crude product on silica gel, petroleum ether (40–60°) serving as eluent, afforded I as yellow needles, m.p. 156 °C (from 1-butanol) in 26% yield. The structure of I (including the site of fluorination) was established by the elemental analyses, the molecular ion at *m/e* 270 in the mass spectrum and the chemical shift and pattern of the ^{19}F NMR-spectrum ($\delta = 132.0$ ppm, singlet)[8]. Compound I is the only fluorobenzo[a]pyrene isomer which should give rise to a ^{19}F NMR singlet. The ^{19}F chemical shift of I closely resembles that of 9-fluoroanthracene ($\delta = 131.8$ ppm)[8]. It should be noted that the ^{19}F NMR-spectrum of the crude reaction mixture did not contain any absorptions which could be attributed to other fluorobenzo[a]pyrene isomers or to addition products. The ^{1}H NMR-spectrum of I lacked the characteristic singlet at 8.42 ppm in the corresponding spectrum of BaP, attributed to H-6[9]. The UV-spectrum of I ($\lambda_{max}^{cyclohexane} = 226$ nm (log ε 4.45), 255 (4.60), 266 (4.62), 275s (4.45), 286 (4.61), 296 (4.74), 336s (3.68), 356 (4.05), 372 (4.29), 383s (4.22), 387 (4.25), 393 (4.28) and 408 (4.60)) is very similar to that of BaP and 4-fluorobenzo[a]pyrene[10]. The formation of I as the predominant product of the fluorination is not surprizing, in view of the enhanced reactivity of position 6 of BaP towards electrophilic reagents[11].



BaP



I

The blocking of the most reactive position of BaP by a fluorine atom, together with the introduction of a fluorine in the neighbourhood of the K-region (C_4–C_5) (but not at the K-region itself) is particularly attractive to structure-activity relationships studies of chemical carcinogenesis in the BaP series[3]. The direct fluorination of BaP with XeF_2 illustrates the applicability of the route to the synthesis of fluorine substituted carcinogenic polycyclic aromatic hydrocarbons[12].

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[8] The ^{19}F NMR-spectra were recorded in dichloromethane at 94.1 MHz. ^{19}F chemical shifts (δ) are reported in ppm, upfield from CCl_3F.

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[12] The direct fluorination of aromatic molecules by xenon difluoride has recently been extended to naphthalene, anthracene, phenanthrene and pyrene. Cf. a) E. D. BERGMANN, H. SELIG, C.-H. LIN, M. RABINOVITZ and I. AGRANAT, J. org. Chem., *40*, 3793 (1975); b) S. P. ANAND, L. A. QUATERMAN, P. A. CHRISTIAN, H. H. HYMAN and R. FILLER, J. org. Chem., *40*, 3796 (1975); c) I. AGRANAT, M. RABINOVITZ, H. SELIG and C.-H. LIN, Chem. Lett., 1271 (1975).

Defensive Substances from Stink Bugs of Cydnidae

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Summary. The odorous and physiologically active substances of the secretions of Japanese stink bugs (Cydnidae) were investigated. The main components of the secretions of *M. japonensis* and *A. nigritus* are *n*-tridecane and *n*-pentadecane together with 2-octenal and 2-decenal, while 2-hexenal is the main components in the secretion of *A. magna*.

In recent years, the nature of pheromone and other considerable chemical release used by insects has aroused considerable interest. Some investigations have been published on the chemical structures or physiological functions of the stink bugs: BLUME et al.[2] reported the presence of 2-heptenal and *n*-tridecane from rice stink bugs, *Oebalus pugnax*. ROTH[3] identified pentanal, heptanal, and octenal from *Scaptocoris divergens* (Cydnidae). WATERHOUSE[4] reported the presence of 2-hexenal, 2-decenal from *Nezara viridula*. 2-hexenal and 2-octenal from *Rhoecocaris sulciventris* and *n*-hexenal from *Mictis profana*. SCHILDKNECHT[5] identified as 2-hexenal, 2-octenal, 2-decanal from *D. baccarum* L. 2-hexenal, 2-octenal from *Eurogaster sp.* and 2-hexenal, 2-octenal, 2-decanal from *P. viridissima*. TSUYUKI et al.[6] reported the following constituents from the stink bugs in Japan: *Nezara viridula* (L.), *trans*-decenal. *Graphosoma rubrolimatum* (Westw.), *trans*-2-decenal, *n*-hexenal. *Aelia fieberi* Scott, *trans*-2-decenal. *Scotinophara lurida* Burmeister, *trans*-2-decenal. *Acanthocoris sordidus* (Thunberg), *n*-hexenal, *trans*-2-hexenal. *Hygica opaca* F., *n*-hexenal. *Plinachtus bicoloripes* Scott, *n*-hexenal, octanal. GILBY et al.[7], *N. viridula* var. *smaregdula*, *trans*-2-propenal, *trans*-2-butenal, methylethyl ketone, ethylpropyl ketone, 4-keto-2-hexene, *trans*-2-hexenal, 4-keto-*trans*-2-hexenal, *trans*-2-hexenyl acetate, *trans*-2-octenal, methylheptyl ketone, *n*-undecane, 4-keto-2-octenal, *trans*-2-octenyl acetate, *n*-undecane, *trans*-2-decenal, *cis*-2-decenal, *n*-tridecane, *trans*-2-decenyl acetate. CALAM et al.[8], *Dysderus inter-*

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[1] The authors are indepted to Dr. NAKAYAMA and Miss EGUCHI (Department of Chemistry, Hiroshima University) for measurement of the mass spectra.

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On the components of the defensive substances of stink bugs

GLC t_R (2-hexenal = 1)	Assigned	*A. magna* composition, %	*M. japonensis*	*A. nigritus*	Method of identification
0.94	unknown	2.7			
1.00	2-hexenal	91.5	11.2		GLC, IR, NMR, 2,4-DNP
1.95	2-octenal	5.8	24.6	4.7	GLC, IR
2.10	*n*-tridecane		61.8	2.0	GLC, MS
2.72	2-decenal		2.4	34.6	GLC, IR, 2,4-DNP
2.82	*n*-pentadecane			58.7	GLC, MS

medius Dist., *n*-dodecane, *n*-tridecane, *n*-pentadecane, hexanal, 2-hexenal, 4-oxo-2-hexen-1-al, 2-octen-1-al, 4-oxo-2-octen-1-al.

Material and method. We have investigated the defensive substances of 3 species of Cydnidae in Japan: *Adrisa magna* Uhler, *Macroscytus japonensis* Scott, *Aethus nigritus* Fabricius. The stink bugs were collected in the ground on April in Hiroshima Prefecture, Japan. The stink bugs were irritated and they then secreted the defensive substance in the test tube. After taking the bugs out of the test tube, the secretion was extracted with *n*-hexane. Evaporation of the solvent gave odorus principles. The ordorus substance of 1.2 mg was obtained from an irritated example of *A. magna,* 0.18 mg of secretion was obtained of *M. japonensis* and 0.08 mg of *A. nigritus.* The idividual components of the secretion were isolated by the preparative gas chromatography using SE30 (10%) column and identified by gas chromatography (GLC), IR-spectrum, NMR-spectrum or mass spectrum (MS) compared with those of authentic specimens. Some of alkenals were further identified by the preparation of 2,4-dinitrophenylphydrazone (2,4-DNP) with Brady's reagent (2,4-dinitrophenylphydrazine). *n*-Alkenals were synthesized from the corresponding *n*-alkanals according to the BEDOUKIAN's method[9]. For analysis Hitachi K53 gas chromatograph equipped with flame ionization detector was used. The gas chromatograph was operated with the temperature programmed from 50 to 160° (3 °C/min) using HB2000 capillary column (0.25 mm × 45 m). The relative percentages of the individual components shown in the Table were determined by integration and summation of the peak areas with electronic digital integrator. Retention time was also determined by the integrator. 2-Hexenal; t_R 1.00 (10.38 min) IR (CCl_4) 2960, 2940, 2880, 2810, 2720, 1690, 1638, 1458, 1381, 1341, 1301, 1280, 1150, 1140, 1090, 1043, 1002, 970 cm^{-1}. NMR (CCl_4); δ 9.50 (1H), 6.86 (1H), 6.07 (1H), 2.30 (2H), 1.45 (2H), 0.93 (3H). 2,4-DNP m.p. 146.5 °C (mixed m.p. not depressed). 2-Octenal; t_R 1.95 IR (CCl_4) 2970, 2945, 2865, 2810, 2725, 1700, 1642, 1475, 1460, 1440, 1385, 1304, 1158, 1144, 1102, 1048, 982 cm^{-1}. 2-Decenal; t_R 2.72 IR (CCl_4) 2962, 2943, 2862, 2725, 1700, 1642, 1472, 1440, 1385, 1300, 1155, 1142, 1100, 978 cm^{-1}. 2,4-DNP m.p. 126.5 °C (mixed m.p. not depressed). *n*-Tridecane; t_R 2.10, MS *m/e* 184 (M^+), 154, 140, 126, 112, 99, 85, 71, 57 (base peak), 43. *n*-Pentadecane t_R 2.82 MS *m/e* 212 (M^+).

Results and discussion. The secretion of *A. magna* contained 2-hexenal (91.5%) and 2-octenal (5.8%) as the main components. The defensive substance of *M. japonensis* identified as 2-hexenal (11.2%), 2-octenal (24.6%) and *n*-undecane (61.8%). *n*-Pentadecane (58.7%) was found in the secretion of *A. nigritus* together with 2-octenal (4.7%), 2-decenal (34.6%) and *n*-tridecane (2.0%). *n*-Alkenal was widely spread through-out Pentatomidae, Coreidae, and Cimex families. The secretion of *M. japonensis* and *A. nigritus* contained the *n*-paraffins as the main components, while no *n*-paraffin was found in the secretion of *A. magna.* These results can be used for the chemosystematic study of the stink bugs. It can be seen that *n*-paraffins in the secretion were used as the solvent of the *n*-alkenals: in the case of *n*-paraffins as the solvent of formic acid in the ants[10].

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NMR-Studies of Triiodothyropropionic Acid in Ethanol-HCl

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Summary. The barrier to rotation in the N-acetyl methyl ester of thyroxine was found to be 8.6 kcal mol^{-1}. Previous experiments determining the barrier to rotation in triiodothyropropionic acid in HCl-ethanol were shown to be in error.

The conformations of the active thyroid hormone 3,5,3'-triiodo-L-thyronine (T_3) have been extensively studied. Steric effects of the 3,5-iodines force the 2 aromatic rings to lie in mutually perpendicular planes (Figure 1), resulting in the formation of 2 conformational isomers which differ only in the orientation of the 3'-iodine with respect to the inner (α) aromatic ring. When the 3'-iodine lies over the α-ring the conformation is termed proximal, and it is distal when the 3'-iodine is away from the α-ring. JORGENSEN et al.[3,4] have con-

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