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THE STRUCTURE OF NEOMATATABIOL, THE POTENT ATTRACTANT FOR CHRYSOPA FROM ACTINIDIA POLYGAMA MIQ.*

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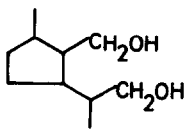
The active components in Actinidia polygama Miq. (Matatabi) for Felidae animals, as previously reported (1), were found to be cyclopentanoid monoterpenes (actinidine, iridomyrmecine, isoiridomyrmecine, dihydronepetalactone, isodihydronepetalactone, neonepetalactone), C_{11}-lactone (actinidiolide, dihydroactinidiolide), and phenylethyl alcohol.

Formerly, Yano (2) Ishimori (3) and Takagi (4) have independently reported the interesting observations that male adults of lacewings, Chrysopa septempunctata Wesmael, Chrysopidae are highly attracted by Actinidia polygama, that is, they swarmed on the leaves and fruits to devour them. Meanwhile, Ishii (5) showed that the neutral extract of the fruits was effectively attractive to the insect. We have recently communicated that one of the attractants contained in fruits is iridodiols (I) (1)

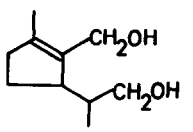
In this communication we would like to report on the structure of neomatatabiol, the extremely potent attractant for Chrysopa.

Isolation from leaves:

The dry leaves were directly steam distilled and the distillate was treated with alkali to remove acidic substances. By the elaborate column chromatography of the neutral fraction on alumina, several grams of crude active alcohol, named neomatatabiol, were obtained from 1000Kg. of fresh leaves. In this case, a small amount of dehydroiridodiol (II) which seems to be a biogenetically important intermediate, was also isolated. By the repeated column chromatography of the crude neomatatabiol, pure neomatatabiol and very small amount of isoneomatatabiol were isolated respectively.



(I)



(II)

It is most remarkable that these monoterpene alcohols were found to be attractive only for the male adults of Chrysopa septempunctata Wesmael and Chrysopa japana Okamoto in the amount of 10^{-6} μg of neomatatabiol and isoneomatatabiol and 10^{-4} μg of dehydroiridodiol.

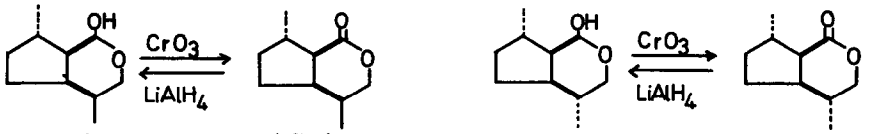
Structure of neomatatabiol and isoneomatatabiol:

Neomatatabiol, $C_{10}H_{18}O_2$, (colorless liquid, b.p. 95°/5mm, $[\alpha]_D^{15}$ +21.3° (C=0.85)) gives positive Tollens test which indicates the presence of potential aldehyde group. However, the IR spectrum of neomatatabiol showed characteristic bands of hydroxyl at 3400 and 1070 cm^{-1} instead of the absence of carbonyl band. By the fact that neomatatabiol affords dihydronepetalactone on chromic acid oxidation, the structure (III) was assigned for neomatatabiol. This assignment was further supported by the N.M.R. spectrum; two doublet methyl signals at 9.20 τ and 9.02 τ (6H, J=6 cps respectively), multiplet signals of CH-CH_2-O- between 6.3 τ and 7.0 τ constituting AB part of an ABX pattern (J_{AX}=10.9 cps; J_{BX}=4.1 cps and J_{AB}=11.2 cps) and a doublet signal of methine between oxygen atoms at 5.7 τ (1H, J=8 cps).

Neomatatabiol was eventually derived from dihydronepetalactone (IV) by the mild reduction with lithium aluminum hydride at -15°.

The reduction of isodihydronepetalactone (VI) with lithium aluminum hydride gave isoneomatatabiol (V) predominantly, the IR spectrum of which differs from that of neomatatabiol, especially in the finger region, but the mass spectrum of isoneomatatabiol was almost identical with that of neomatatabiol. The N.M.R. spectrum of isoneomatatabiol shows the presence of two doublet methyls at 9.20 τ and 8.95 τ, multiplet methylene of a -O-CH_2-CH- group centered at 6.5 τ and doublet at 4.92 τ (J=2 cps) attributed to a -O-CH-O group.

From the above chemical and spectroscopic evidences the structure of isoneomatatabiol was represented by (V).



(III) (IV) (V) (VI)

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References

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1. T. Sakan, A. Fujino, F. Murai, A. Suzui and Y. Butsugan, Bull. Chem. Soc. Japan 32, 1154 (1959); T. Sakan, A. Fujino and F. Murai, Nippon Kagaku Zasshi, 81, 1320 (1960); F. Murai ibid., 81, 1324 (1960); A. Fujino, ibid., 81, 1327 (1960); T. Sakan, S. Isoe, S. B. Hyeon, T. Ono and I. Takagi, Bull. Chem. Soc. Japan 37, 1888 (1964); T. Sakan, S. Isoe, S. B. Hyeon, R. Katsumura, T. Maeda, J. Wolinsky, D. Dickerson, M. Slabaugh and D. Nelson, Tetrahedron Letters 4097 (1964); T. Sakan, S. Isoe and S. B. Hyeon, Tetrahedron Letters 1623 (1967).
2. M. Yano, Kontyu, 5, 96 (1931).
3. N. Ishimori, ibid., 5, 96 (1931).
4. G. Takagi, Zool, Mag., 44, 477 (1932); G. Takagi, Nogyo, No.802, 33 (1950).
5. S. Ishii, Jap. J. Appl. Ent, Zool. 8, 334 (1964).