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[Lab. of Herbal Garden]

**Pharmacognostical Studies on the Chinese Crude Drug "Tougucao" (1)
Botanical Origin of the Chinese Crude Drug "Tougucao" Derived from
Vicia Plants Produced in Heilongjiang Province.**

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The whole plants of the genus *Vicia* plants have been commonly used as the source of the traditional Chinese crude drug "Tougucao(とうこつそう)" in the northeast area of China, whereas shredded leguminous plants were used as the crude drug "Tougucao" in Heilongjiang province. A comparative anatomical study was performed on the stems and leaflets of 6 medicinal *Vicia* species collected in Heilongjiang province. Thirteen commercial Tougucao samples were examined and their botanical origins were determined to be mostly 2 *Vicia* species, *Vicia amoena* and *V. pseudo-orobus*.

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**Pharmacognostical Evaluation of Arctii Fructus (2)
Adulteration on the Chinese Commercial Samples.**

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Samples of Arctii Fructus, fruits of *Arctium lappa*, commercially obtained in various provinces of China were found to be adulterated with fruits of five species, *Arctium tomentosum*, *Silybium marianum*, *Amorpha fruticosa*, *Onopordum acanthium* and *Aucklandia lappa*. HPLC revealed that the chemical compositions of the fruits of *Ar. tomentosum* was very similar composition to that of *Arctium lappa*, the origin plant of Arctii fructus. The fruits of *O. acanthium* and *Au. lappa* contained arctiin, but their chemical compositions were slightly different from that of *Ar. lappa*. The fruits of *S. maritimum* and *Am. fruticosa* showed quite different HPLC profiles.

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[Lab. of Manufacturing Pharmacy]

Novel Polar Cycloaddition of 1,2-Thiazinylium Salt.

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Tatsunori IWAMURA

Dibenzo[*c,e*][1,2]thiazinylium tetrafluoroborate, generated *in situ* from the reaction of dibenzo[*c,e*][1,2]thiazine 5-oxide with trifluoroacetic anhydride in the presence of lithium tetrafluoroborate in dichloroethane, underwent polar cycloaddition with several 1,3-butadienes to afford new sulfur-nitrogen-containing sulfonium heterocycles in good yields. The cycloaddition with unsymmetrical 1,3-butadiene, isoprene afforded two regioisomeric cycloadducts in a ratio of 3.5:1, showing different results compared to those of dibenzo[*c,e*]thiopyrylium salt described in our previous report. Deprotonation of the cycloadduct underwent ring transformation to yield a pyrrole derivative.

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[Lab. of Manufacturing Pharmacy]

**Polar Cycloaddition of Monocyclic 1,2-Thiazinylium Salt and Transformation
of the Cycloadducts to 1,2-Azathiabenzenes.**

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A new monocyclic 1,2-thiazinylium salt, 4,5-diphenyl-1,2-thiazinylium perchlorate was successfully synthesized by treatment of 4,5-diphenyl-5*H*-1,2-thiazine with sulfuryl chloride, followed by addition of 70% perchloric acid. The perchlorate has two possible different active bonds (C=S⁺ and N=S⁺ bonds) for the cycloaddition. Thus, addition of several 1,3-butadienes to the perchlorate resulted exclusively in the formation of the product cycloadduct across the C=S⁺ bond, but no cycloadduct across the N=S⁺ bond was obtained. This complete regioselectivity was rationalized in terms of Frontier Molecular Orbital coefficients. Deprotonation of the cycloadducts with a strong base provided novel 1,2-azathiabenzenes having sulfur at a bridgehead position as yellow crystals together with spiro compounds which would have been formed *via* sigmatropic rearrangement of the sulfonium ylides.