identified with the synthetic samples as methiodides of m.p. 270° (decomp.) and m.p. 203~204.5°, respectively. The former was synthesized by the Wolff-Kishner reduction of 3-methyl-3-azabicyclo[3.2.1]octan-8-one and the latter by the method of Rice and Grogan.[7] Based on these facts, the structure of XII was designated as 2-methyl-2-azatricyclo[5.1.0.$0^{4,8}$]octane.

In these reactions, reaction by-products were also investigated in both azabicyclononane and -octane compounds, but any products corresponding to an isomer of the tricyclic amine (II or XII) could not be isolated. Consequently, it was concluded that the insertion reaction of these carbenes, which are supposed as intermediates in these reactions, proceeds uniquely into the opposite side of N-methyl group in the case of azabicyclononane system and into the same side in the case of azabicyclo-öctane.

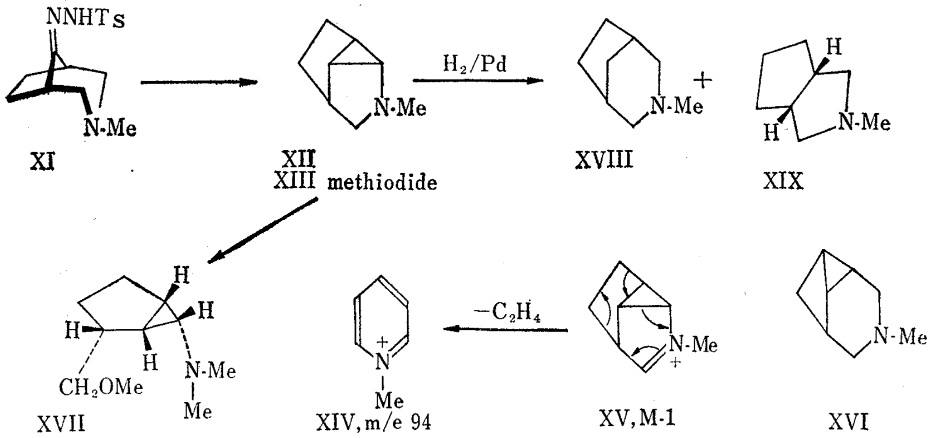

Chart 2.

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[7] L.M. Rice, C.H. Grogan: J. Org. Chem., **24**, 7 (1959).

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The Sapogenin Constituent of the Seeds of *Camellia sasanqua* Thunb.

In relation to the study on theasapogenols[1~4] obtained from the seeds saponin of *Thea sinensis* L. (Japanese name: cha), hitherto engaged in this laboratory, we have

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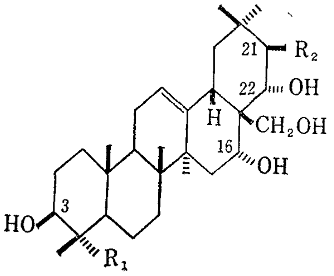
[1] I. Yosioka, T. Nishimura, A. Matsuda, I. Kitagawa: Tetrahedron Letters, **1966**, 5973.
[2] *Idem*: *Ibid.*, **1966**, 5979.
[3] I. Yosioka, A. Matsuda, T. Nishimura, I. Kitagawa: Chem. & Ind. (London), **1966**, 2202.
[4] I. Yosioka, T. Nishimura, A. Matsuda, K. Imai, I. Kitagawa: Tetrahedron Letters, **1967**, 637.
[5] S.R. Chakrabarty, M.M. Chakrabarty: Indian Soap J., **20**, 16 (1954) (C.A., **49**, 16469 (1955)).

planned some comparative studies on the sapogenin constituents of several plant materials belonging to *Theaceae* family. The present communication describes the sapogenin constituent of the seeds of *Camellia sasanqua* Thunb. (Japanese name : sazanka). Although the work on its fat component has been known in the literature,[5] no investigation concerning to the saponin has ever appeared.

On treatment by the usual butanol-water fractionation procedure followed by repeated ether washings, the methanol extract of the defatted seeds furnished crude sasanqua-saponin (with a yield of 8.5% from the defatted seeds). The latter yielded a sapogenin mixture by acid hydrolysis (refluxed for 5 hours in 5% methanolic sulfuric acid) followed by an alkaline treatment (refluxed for 1 hour in 5% methanolic potassium hydroxide). Thin-layer chromatography (TLC) disclosed that the genin mixture consisted of several triterpenoid components, among which six triterpenoids designated according to their Rf values on TLC from the top as S-I, S-Ⅱ, S-Ⅲ, S-Ⅳ, S-Ⅴ and S-Ⅵ were successfully isolated by repeated column chromatography on neutral alumina and preparative silica gel TLC with the approximate yields of 10%, 1%, 1%, 1%, 2% and 30% respectively (based on the starting genin mixture). In comparison of the physical properties (m.p., TLC, and infrared spectra) of these triterpenoids with the known camellia-sapogenols[6] and theasapogenols, the following respective identities were confirmed : S-I with camellia-sapogenol I (1), S-Ⅱ with camellia-sapogenol Ⅱ (2), S-Ⅳ with theasapogenol B (3),[1] S-Ⅴ with theasapogenol E (4),[3] and S-Ⅵ with theasapogenol A (5).[2] Camellia-sapogenols I and Ⅱ are main sapogenols of the seeds of *Camellia japonica* L. (Japanese name : tsubaki), whereas theasapogenols A, B, and E are the majors of the seeds of *Thea sinensis* L. The chemical structure of S-Ⅲ is now under investigation.



1) $R_1=CH_3$, $R_2=H$ camellia-sapogenol I
2) $R_1=CHO$, $R_2=H$ camellia-sapogenol Ⅱ
3) $R_1=CH_3$, $R_2=OH$ theasapogenol B (=barringtogenol C)
4) $R_1=CHO$, $R_2=OH$ theasapogenol E
5) $R_1=CH_2OH$, $R_2=OH$ theasapogenol A

Chart 1.

Botanically, *C. sasanqua* Thunb. situates closely related to *C. japonica* L.and *T. sinensis* L., and it is interesting from the chemotaxonomical viewpoint to note that *C. sasanqua* seeds contain in rich amount both of the major sapogenols of two related species.

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6) T. Murakami, H. Itokawa, H. Sawada : The 10th Symposium on the Chemistry of Natural Products (Tokyo, Oct. 6~8, 1966), Symposium Papers, p. 278; S. Ito, M. Kodama, M. Konoike, T. Ogino : *Ibid.*, p. 270.