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Chemical diversity of the genus *Caesalpinia* (Fabaceae): new types of cassane diterpenes from *Caesalpinia crista*

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The genus *Caesalpinia* is known to consist of more than 100 species. Though it constitutes a relatively large group in the family Fabaceae, chemical studies are limited to a few species among those. As far as results of chemical research undertaken so far are concerned, it seems that they are divided into two groups based on constituents: the one such as *C. sappan* is predominated by homoisoflavonoids, and the other such as *C. bonduc* by furano-cassane diterpenes. We conducted chemical investigation on *C. bonduc* of Southeast Asian origin and reported the occurrence of a new type of hemiacetal cassanes fused with not a furan but an α,β -butenolide ring (5-hydroxyfuran-2(5H)-one), for which new names of neocaesalpin series are proposed. The previous chemical investigation on the same species that is exclusively of American origin revealed only the presence of furano-cassanes to which serial names of caesalpin are given. There will be two possible accounts for these results as follows. One is that an α,β -butenolide ring is artificial arising from addition of singlet oxygen on furan during either extraction or purification process, and the other is that those possessing an α,β -butenolide ring are not artificial but derived from a distinguished chemical race of *C. bonduc* which occurs widely in both the tropics and subtropics in the world. Our interest in cassanes featuring distinguished structural diversity instigated us to focus on other botanical sources. *C. crista* is one of four species of the genus *Caesalpinia* occurring in Japan, and chemical studies on the leaves of this species collected in the Rykyus furnished new neocaesalpin analogues named Neocaesalpins H and I. However, those belonging to neocaesalpin group are obtained almost exclusively by our group. We are thus forced to consider the possibility of neocaesalpins being artificial, and carefully reinvestigated *C. crista* and *C. bonduc* using new plant materials collected in the same place. These studies furnished the isolation of two additional new compounds from the former species: one is a new type of nor-cassane fused with an ordinary furan, and the other is a 12-deoxy form of Neocaesalpin H. The latter compound biosynthetically requires one more deoxygenation step that follows the possible oxygenation of a furan ring. Therefore, its isolation is of particular interest since it completely eliminates the possibility of neocaesalpins being artificial. Though the number of cassanes isolated from the corresponding *Caesalpinia* species by our group is small, it revealed the distinguished chemical diversity based not only on the intra-specific differentiation of *C. bonduc* but also on the inter-specific differentiation among the genus *Caesalpinia*, indicating that they are the promising source of new types of chemicals. During a search of phytochemical literatures concerning

Caesalpinia

505species, the confused use of botanical names has often been encountered. What are referred to as *C. bonduc* and *C. crista* in our study is *C. bonduc* (L.) Roxb. emend. Dandy et Exell and *C. crista* L. emend. Dandy et Exell, respectively.