THE QUESTION OF THE CONFIGURATIONS OF FARNESIFEROL A, GUMMOSIN, BADRAKEMIN, AND COLLADONIN

M. E. Perel'son, N. P. Kir'yalov,
and A. I. Ban'kovskii

UDC 547.9 : 582.89

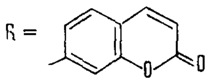
The structure and absolute configuration of farnesiferol A were established mainly by chemical methods and the ORD method [1]. However, the configuration at $C_{1'}$ was not shown unambiguously; the authors concerned suggested the axial orientation for the $C_{1'}-CH_2$ group. Other workers [2], by analogy with other diterpenoids postulated the equatorial orientation of the $C_{1'}-CH_2$ group in the farnesiferol A molecule.

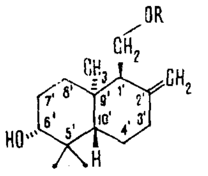
It has been shown that another terpenoid coumarin, gummosin, is an epimer of farnesiferol A at $C_{6'}$ [3]; the $C_{6'}$ hydroxy group in gummosin is axial and in farnesiferol A it is equatorial.

For another pair of epimers at $C_{6'}$, badrakemin [4, 5] and colladonin [6], the nature of the linkage of the decalin rings had not been established and the configuration at $C_{1'}$ had not been shown.

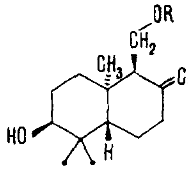
In order to answer the question of the configurations of these compounds definitively, we have studied their NMR spectra using europium tris(dipivaloylmethanate) as a shift reagent. As a result we have been able to show that badrakemin and colladonin have a trans-decalin ring system, and the $C_{1'}-CH_2$ group in farnesiferol A and gummosin is axial and in badrakemin and colladonin it is equatorial.

Thus, the structures of all four isomers can be represented in the following way (for badrakemin and colladonin the formulas of their mirror images are given):

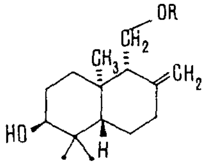




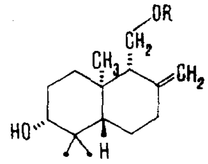
Farnesiferol A



Gummosin



Badrakemin



Colladonin

The stereochemistry of the compounds given above has been discussed in previous papers [7-9], but in these, on the basis of spectral and chemical data, erroneous configurations of gummosin and badrakemin were proposed and it was incorrectly concluded that colladonin and farnesiferol A were identical. The correlations between the parameters of the PMR spectra and the stereochemistry of terpenoid coumarins established by Saidkhodzhaev and Nikonov [7] likewise do not correspond to the facts.

All-Union Scientific-Research Institute of Medicinal Plants. V. L. Komarov Botanical Institute, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 244-245, March-April, 1975. Original article submitted June 6, 1974.

The physicochemical characteristics of a coumarin published under the name of "mogoltadin" [9] show that this compound is identical with farnesiferol A.

A detailed account of all the experimental facts will be given in a full communication.

LITERATURE CITED

1. L. Caglioti, H. Naef, D. Arigini, and O. Jeger, Helv. Chim. Acta, 41, 2278 (1958).
2. A. I. Scott, F. McCapra, F. Comer, S. A. Sutherland, D. W. Young, G. A. Sim, and G. Ferguson, Tetrahedron, 20, 1339 (1964).
3. N. P. Kir'yalov and S. D. Movchan, Khim. Prirodn. Soedin., 383 (1966).
4. N. P. Kir'yalov, Khim. Prirodn. Soedin., 363 (1967).
5. V. Yu. Bagirov, N. P. Kir'yalov, V. I. Sheichenko, and V. N. Bochkarev, Khim. Prirodn. Soedin., 466 (1970).
6. A. I. Ban'kovskii, N. E. Ermatov, M. E. Perel'son, L. Bubeva-Ivanova, and N. St. Pavlova, Khim. Prirodn. Soedin., 173 (1970).
7. A. I. Saidkhodzhaev and G. K. Nikonov, Khim. Prirodn. Soedin., 490 (1973).
8. A. I. Saidkhodzhaev and G. K. Nikonov, Khim. Prirodn. Soedin., 15 (1974).
9. T. Kh. Khasanov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 25 (1974).