15. V. M. Easterwood and B. J. L. Huff, Svensk Papperstidn., 72, 768 (1969).
16. H. Björndal, B. Lindberg, and S. Svenson, Acta Chem. Scand., 21, 1801 (1967).

SOME ASPECTS OF THE STEREOCHEMISTRY AND NOMENCLATURE OF POLYUNSATURATED HYDROXY FATTY ACIDS

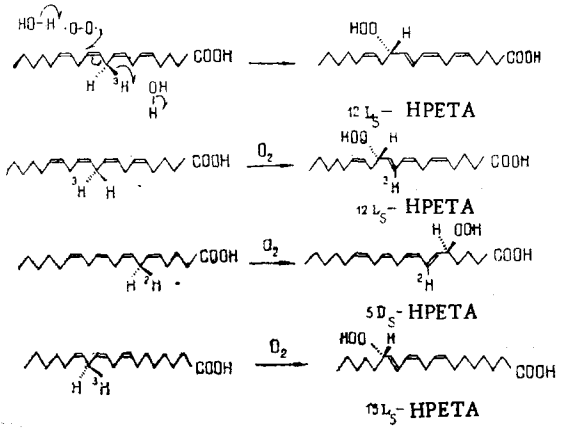
A. G. Panosyan

UDC: 547.475.02:541.63

When the D, L (but not the R, S) nomenclature is used, general laws are observed in the stereochemistry of lipoxygenase oxidation reactions and in the formation of epoxides from hydroperoxides of polysaturated hydroxy fatty acids. In both cases the formation of a C—O bond is coupled with the stereoselective elimination of a hydrogen atom, and the chiral and prochiral carbon atoms have identical configurations. The use of the D, L nomenclature in the polyenic hydroxy fatty acid series appears preferable to that of the R, S nomenclature.

In a study of the lipoxygenase oxidation of unsaturated fatty acids, a rule has been found which relates to the stereochemistry of the inclusion of an oxygen atom and the elimination of hydrogen [1-7]. The formation of hydroxy acids with the L configuration of the asymmetric center is accompanied by the stereoselective elimination of a tritium atom present in prochiral centers with the pro-L-configurations in the molecules of radioactively labeled fatty acids [1-4, 6, 7].

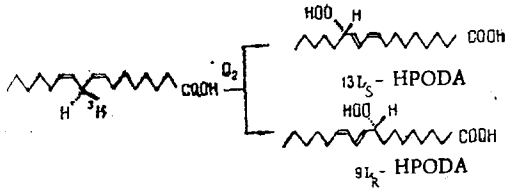
Analogously, the lipoxygenase oxidation of $7L_R$-^3H (or ^2H)-arachidonic acid leads to the formation of 5-D_S-HPETA quantitatively containing the whole of the isotopic label, which indicates a stereoselective elimination of the 7D_S hydrogen atom [5-7]. The inclusion of an oxygen atom and the elimination of a hydrogen atom take place in opposite directions from the plane in which the carbon atoms of the penta-cis-1, cis-4-diene grouping are located with a fixed conformation of the C—C bonds, as shown in scheme 1*.



*Abbreviations: 12L_S-HPETA — (12S)-12-hydroperoxyeicosa-5Z, 8Z, 10E, 14Z-tetraenoic acid; 15L_S-HPETA — (15S)-15-hydroperoxyeicosa-8Z, 11Z, 13E-trienoic acid; 5D_S-HPETA — (5S)-5-hydroperoxyeicosa-6E, 8Z, 11Z, 14Z-tetraenoic acid; 5D_S-HPETA — (5S)-5-hydroperoxyeicosa-6E, 8Z, 11Z, 14Z, 17Z-pentaenoic acid; 9L_R-HPODA — (9R)-hydroperoxyoctadeca-10E, 12Z-dienoic acid; 13L_S-HPODA — (13S)-13-hydroperoxyoctadeca-9Z-11E-dienoic acid.

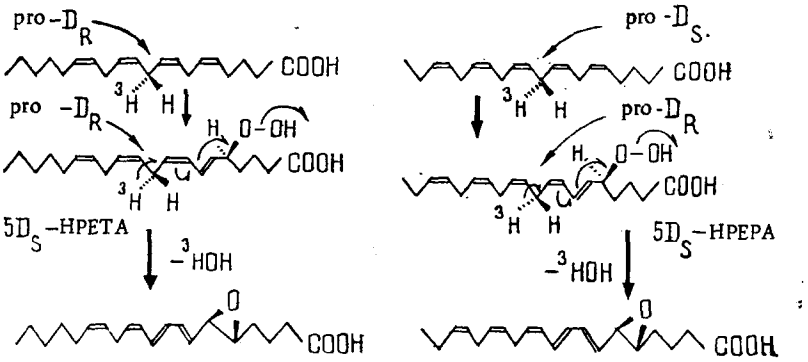
A. L. Mndzhoyan Institute of Fine Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 622-623, September-October, 1985. Original article submitted December 5, 1984.

 0009-3130/85/2105-0582$09.50



Scheme 1

The same rule is observed in reactions forming 5,6-trans-epoxides (leukotrienes A_4 and A_5) from hydroperoxy acids (5D$_S$-HPETA and 5D$_S$-HPEPA, respectively). Here tritium atoms are eliminated from pro-D carbon atoms in the molecules of the hydroperoxy acids with the 5D configuration of the asymmetric center and form epoxides having the D configuration at C-5-6 [6-8].



Leukotriene A_4 Leukotriene A_5

If we keep the conformations of the C–C bonds shown above and use the D, L (but not the R, S) nomenclature for the chiral and prochiral centers, the elimination of hydrogen from a prochiral L-carbon atom always leads to the L configuration of the carbon atom bearing oxygen, and conversely.

The use of the D, L nomenclature in the case of the hydroxy derivatives of polyenic fatty acids is obviously more desirable than that of the R, S nomenclature, since it permits an avoidance of the misunderstandings that arise in connection with a change in the number of double bonds in the carbon skeleton, such as, for example:

(9D$_R$)-9-Hydroxyoctadecanoic Acid (9D$_S$)-9-Hydroxyoctadecanoic-10E, 13Z-dienoic Acid

SUMMARY

1. In the polyenic hydroxy fatty acid series the use of the D, L nomenclature is preferable to that of the R, S nomenclature.

2. In lipoxygenase oxidation reactions and in the formation of epoxides, a common relationship exists between the configuration of the asymmetric carbon atom and the stereochemistry of the elimination of a hydrogen atom.

LITERATURE CITED

1. M. Hamberg and G. Hamberg, Biochem. Biophys. Res. Communs., 95, 1090 (1980).
2. M. Hamberg and B. Samuelsson, Biochim. Biophys. Acta, 617, 545 (1980).

3. M. Hamberg and B. Samuelsson, J. Biol. Chem., 242, 5329 (1967).
4. M. R. Egmond, J. F. G. Vliegenthart, and J. Boldingh, Biochem. Biophys. Res. Communs., 48, 1055 (1972).
5. E. J. Corey and R. T. Lansbury, Jr., J. Am. Chem. Soc., 105, 4093 (1983).
6. A. G. Panossian, M. Hamberg, and B. Samuelsson, FEBS Lett., 150, 511 (1982).
7. R. L. Mass, C. D. Ingram, D. F. Taber, J. A. Oates, and A. R. Brash, J. Biol. Chem., 257, 13525 (1982).
8. S. Hammarström, J. Biol. Chem., 258, 1427 (1983).

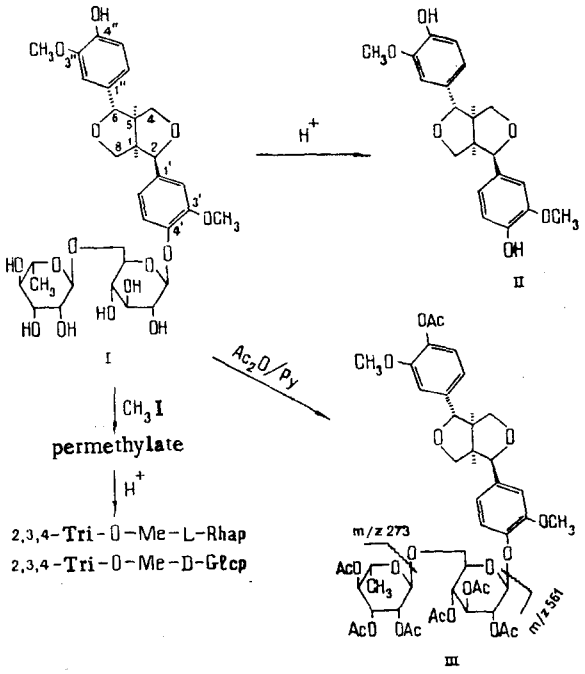
VERSICOSIDE — A NEW LIGNAN GLYCOSIDE FROM *Haplophyllum versicolor*

É. Kh. Batirov, A. D. Matkarimov,
V. M. Malikov, and M. R. Yagudaev

UDC: 547.639

A new lignin glyocoside has been isolated from *Haplophyllum versicolor* and has been called versicoside. It has been established by chemical and spectral methods that verscioside is (+)-epipinoresinol 4'-O-[O-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside].

Continuing a study of components of the plant of the genus *Haplophyllum* A. Juss, we have investigated the epigeal part of *Haplophyllum versicolor* Fisch. et Mey. growing on the Ustyurt plateau. Chromatographing an ethanolic extract on a column of silica gel in the chloroform–methanol system led to the isolation of a new glycoside, which we have called versicoside. Versicoside (I) is an optically active phenolic compound with the composition $C_{32}H_{42}O_{15}$. Its IR spectrum contains absorption bands of hydroxy and methoxy groups, of aromatic C=C bonds, and of the C–O vibrations of glycosides. The UV spectrum of (I) has maxima at 230 and 280 nm, which shows the presence of hydroxybenzene rings in the molecule



Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 624-628, September-October, 1985. Original article submitted November 28, 1984.

 0009-3130/85/2105-0584$09.50