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CHEMICAL TRANSFORMATIONS OF NEOLIGNANS

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Neolignans, generated by oxidative dimerization of propenylphenol and/or allylphenol, undergo further modifying steps. These biosynthetic reactions, confirmed in vitro, *include Cope, retro-Claisen and Claisen rearrangements. Additionally acid catalysis effects conversions of bicyclo [3.2.1] octanoid neolignans into hydrobenzofuranoid neolignans, or inversely of hydrobenzofuranoid neolignans into bicyclo [3.2.1] octanoid neolignans, of hydrobenzofuranoid neolignans into futoenone type neolignans, of tetrahydrofuran neolignans into aryltetralin neolignans, as well as modifications by Friedel – Crafts reactions and the transformation of aryltetralin neolignans into arylindanones by pinacoline – pinacolone type rearrangement.*

Key words: neolignans – chemistry – rearrangements – chiroptical properties

Neolignans are defined as dimers of C_6-C_3 unities. Different coupling modes of these unities afford diverse skeleta. Further modifying steps increase the number of neolignans. A review (Gottlieb & Yoshida, 1989) describes the occurrence in plants of 320 neolignans belonging to 42 skeleta. In spite of these numbers, few chemical reactions of neolignans are registered in the literature. Some transformations were carried out in order to evidence biogenesis of these compounds. Besides, a number of conversions were performed aimming structural elucidations.

Postulated biosynthesis for benzofuran neolignans isolated from *Nectandra miranda* (Aiba et al., 1977) were confirmed *in vitro*. The reaction sequences include Cope, retro-Claisen and Claisen rearrangements (Fig. 1).

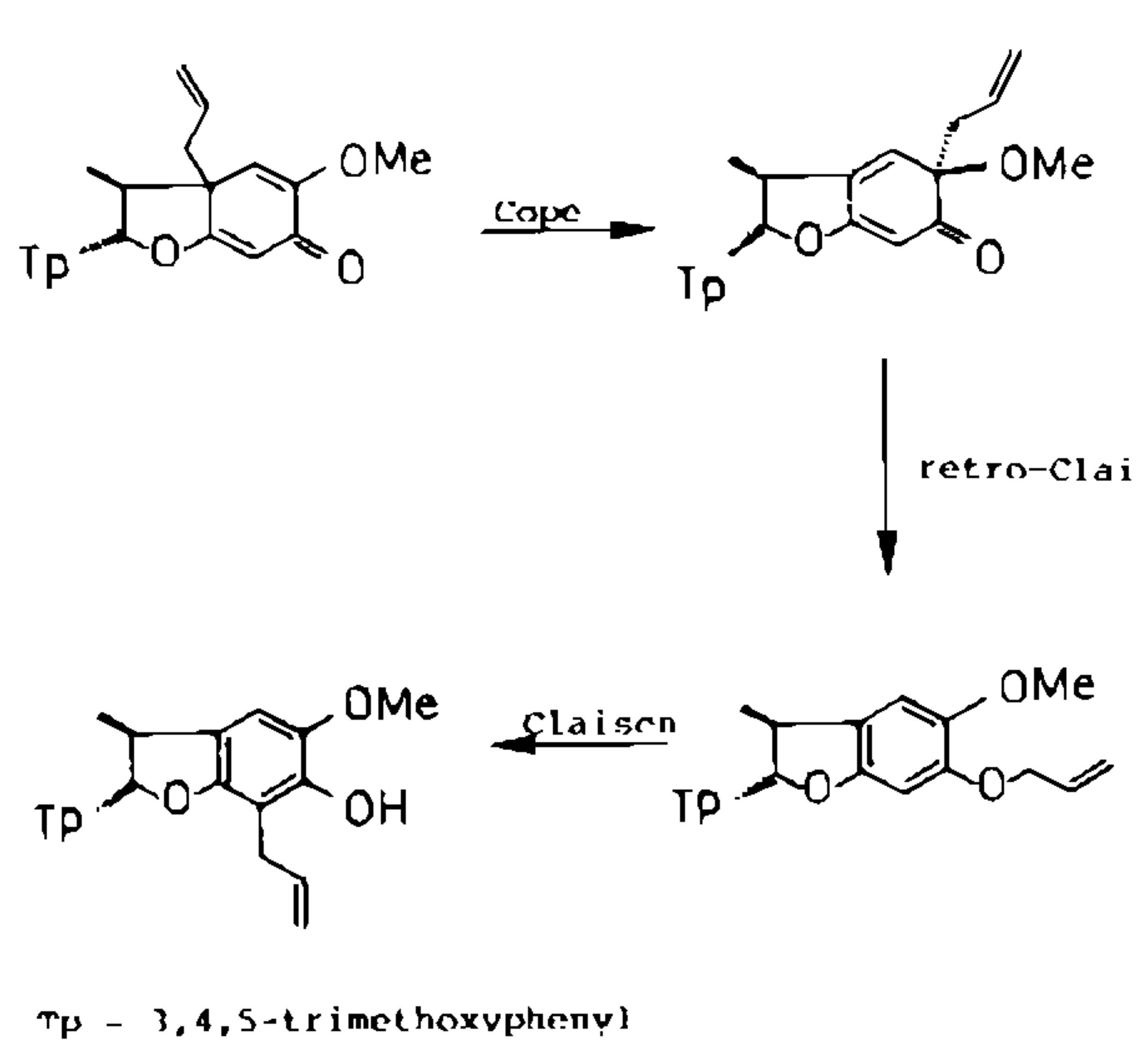

Fig. 1: rearrangements of benzofuran neolignans.

Neolignans isolated from fruits of *Virola sebifera* (Lopes et al., 1984b) can be biosynthetically rationalized through Friedel-Crafts and retro-Friedel-Crafts reactions (Fig. 2).

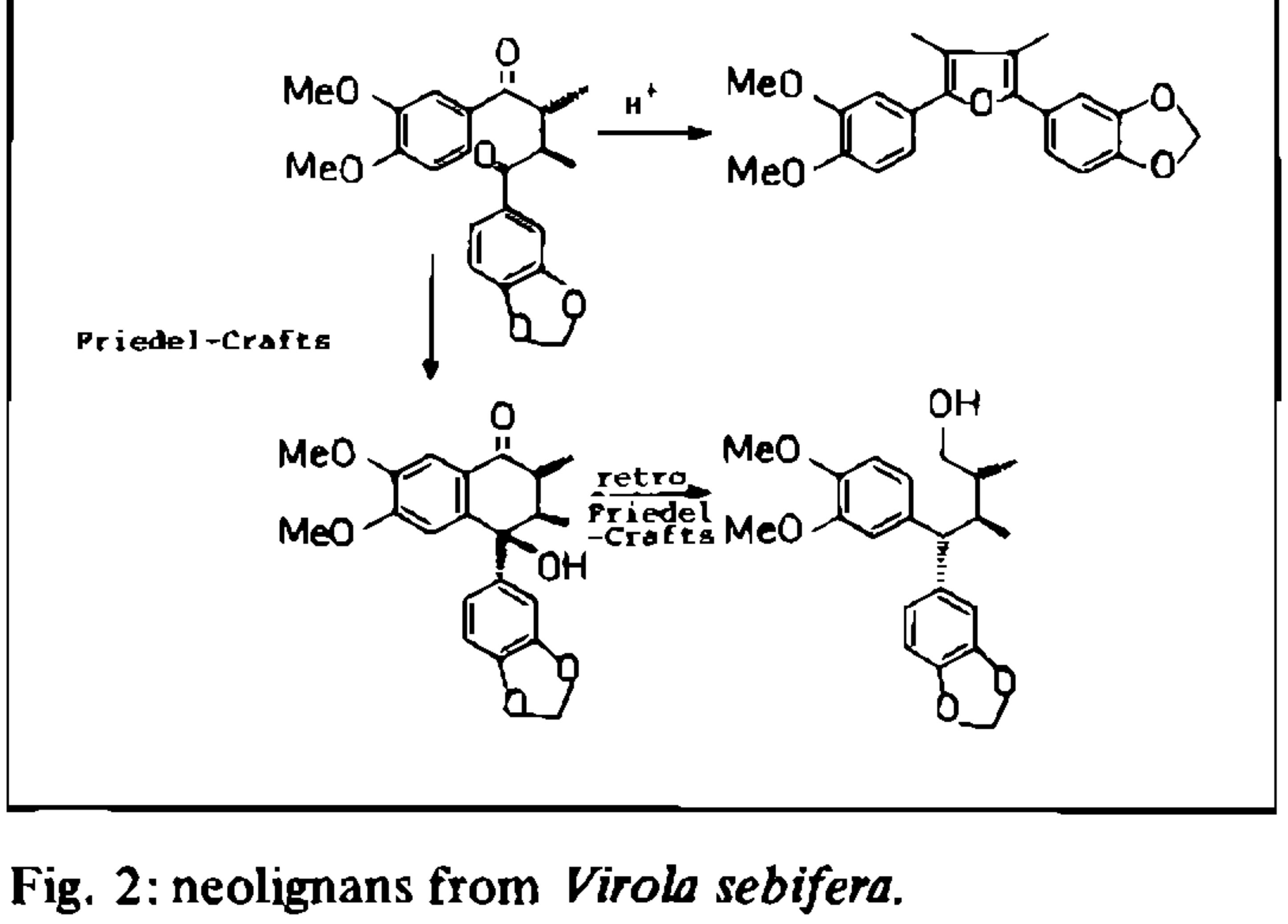

Fig. 2: neolignans from *Virola sebifera.*

Conversions of trihydroxyaryltetralone neolignan into arylindanones by Wagner-Meerwein rearrangements were postulated as biosynthetic pathway (Lopes et al., 1984a) (Fig. 3).

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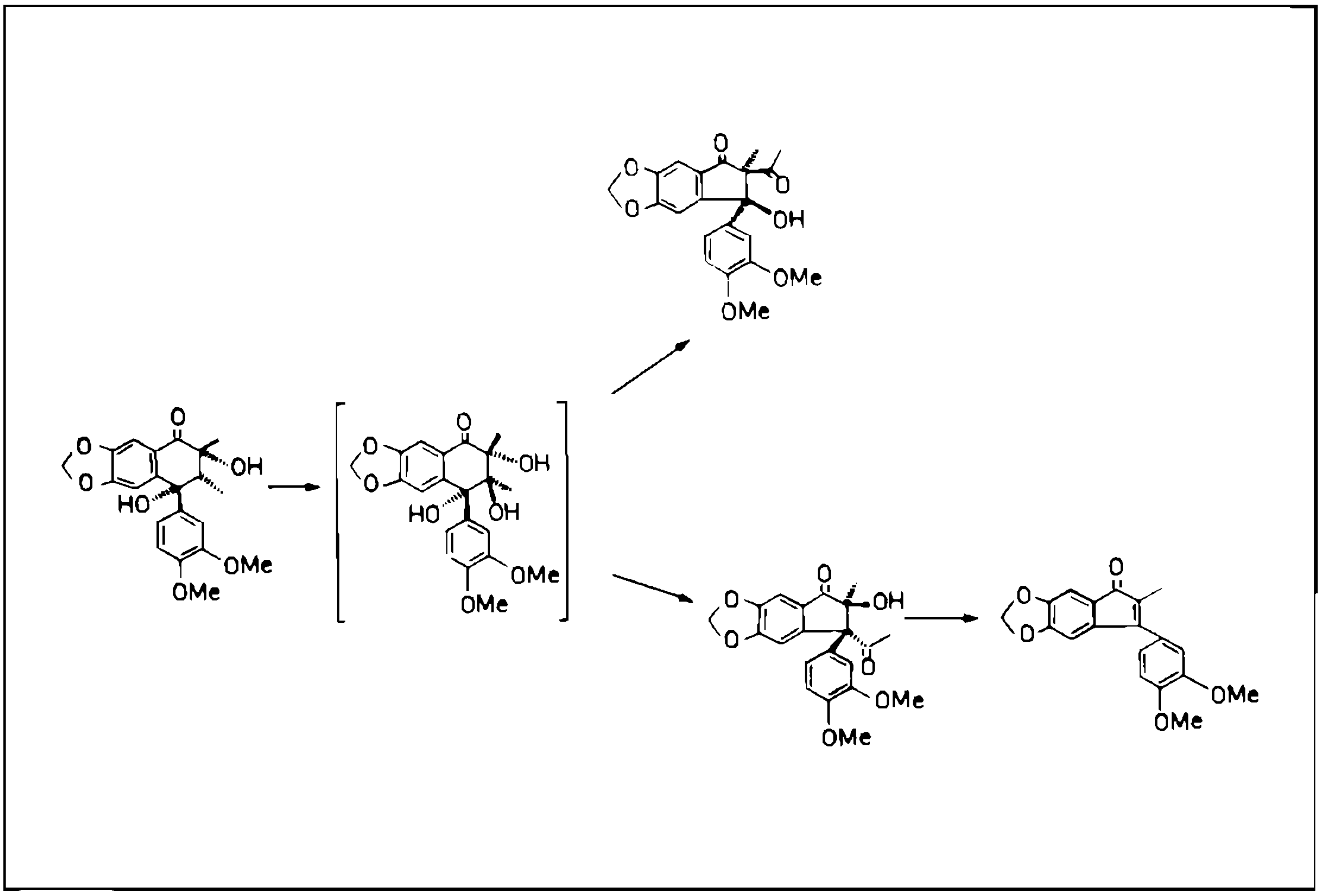


Fig. 3: Wagner-Meerwein rearrangements.

A specimen of *Ocotea porosa* collected at Instituto Botânico (São Paulo-SP) afforded, by chromatographic treatments, a hexahydrobenzofuran neolignan designated porosin. Further analysis of the same material showed the occurrence of other benzofuran neolignans (Dias et al., 1986) (Fig. 4).

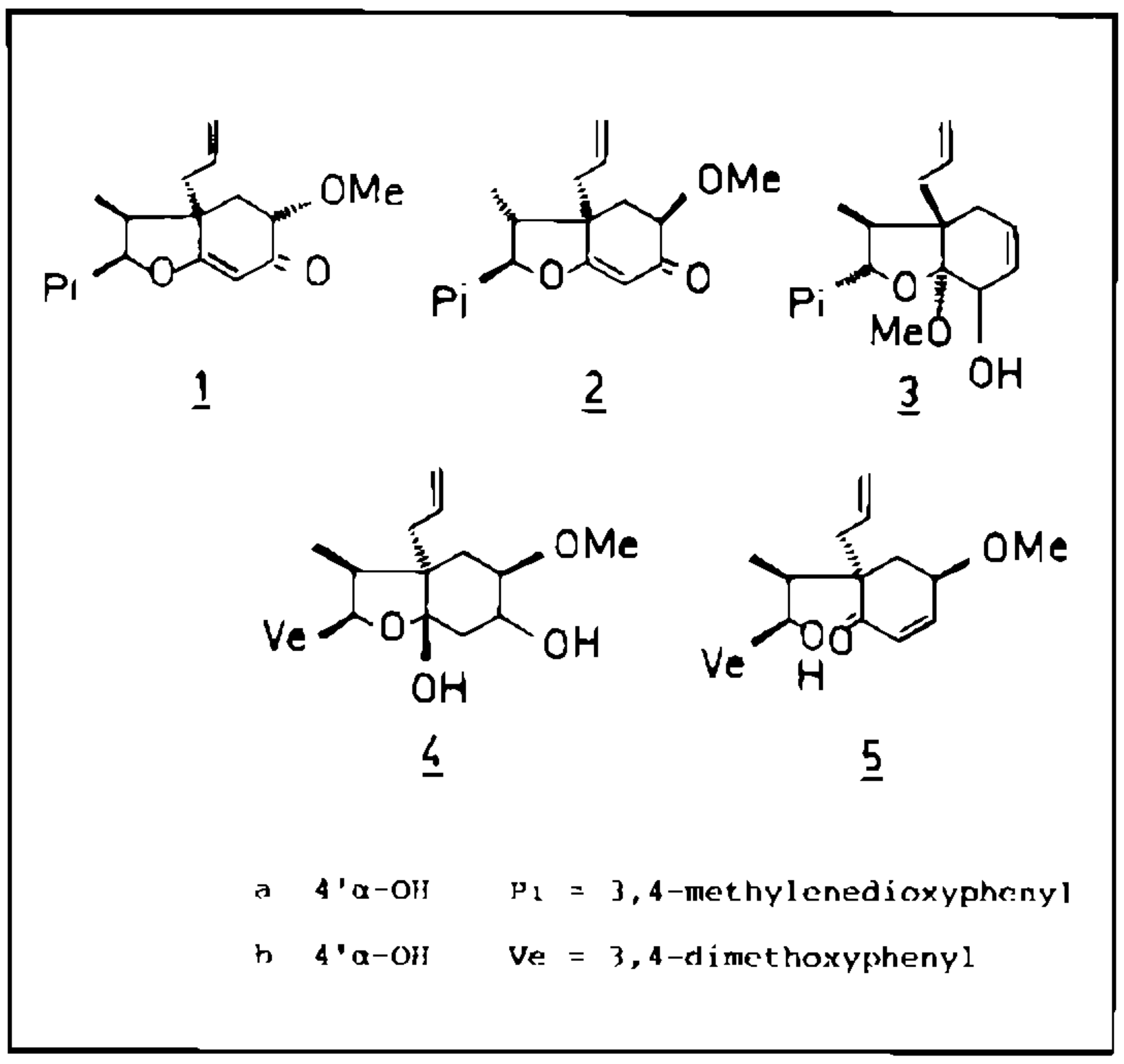


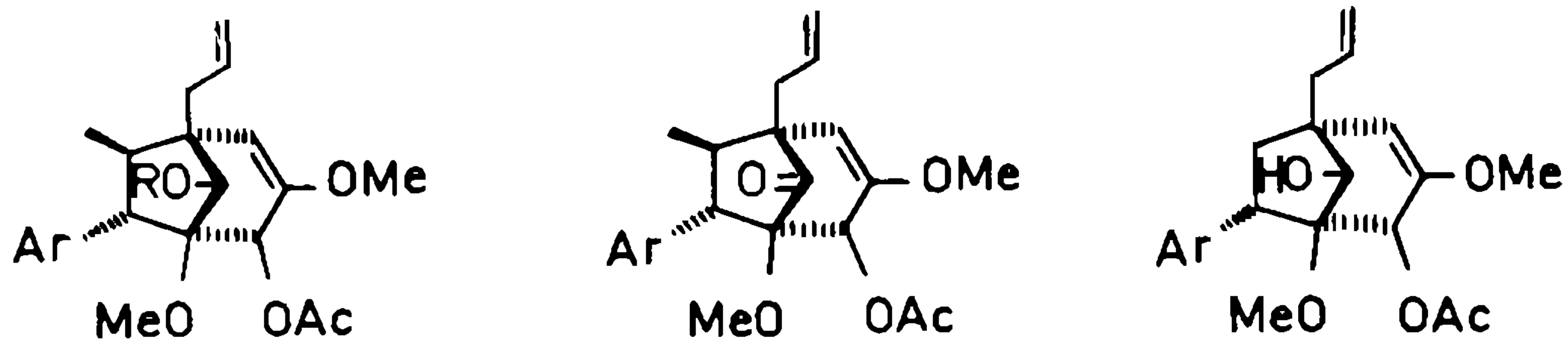
Fig. 4: benzofuran neolignans from *Ocotea porosa*.

Ocotea porosa collected around Cunha (SP) yielded, under similar fractionation procedures, only bicyclooctane neolignans (Gomes et al., 1983) (Fig. 5).

Skeletal interconversions of benzofuran and bicyclooctane were observed *in vitro* by acid catalysis (Büchi & Mak, 1977; Alvarenga et al., 1978). These processes can be involved in specimens of *Ocotea porosa*. (Fig. 6).

Absolute configuration was evidenced by comparison between ORD or CD curves of isolated neolignans and those of model compounds (Gottlieb et al., 1977).

Absolute configuration of octahydrobenzofuran, megaphone type (Carvalho et al., 1988), futoenone type (Dias et al., 1982) and magnostellin (Kato et al., 1986) neolignans was also determined through chiroptical analysis of compounds with established stereochemistries obtained by chemical transformations (Figs 7, 8 9).



1

a Ar = Pi, R = H
b Ar = Mp, R = H
c Ar = Mp, R = Ac

2

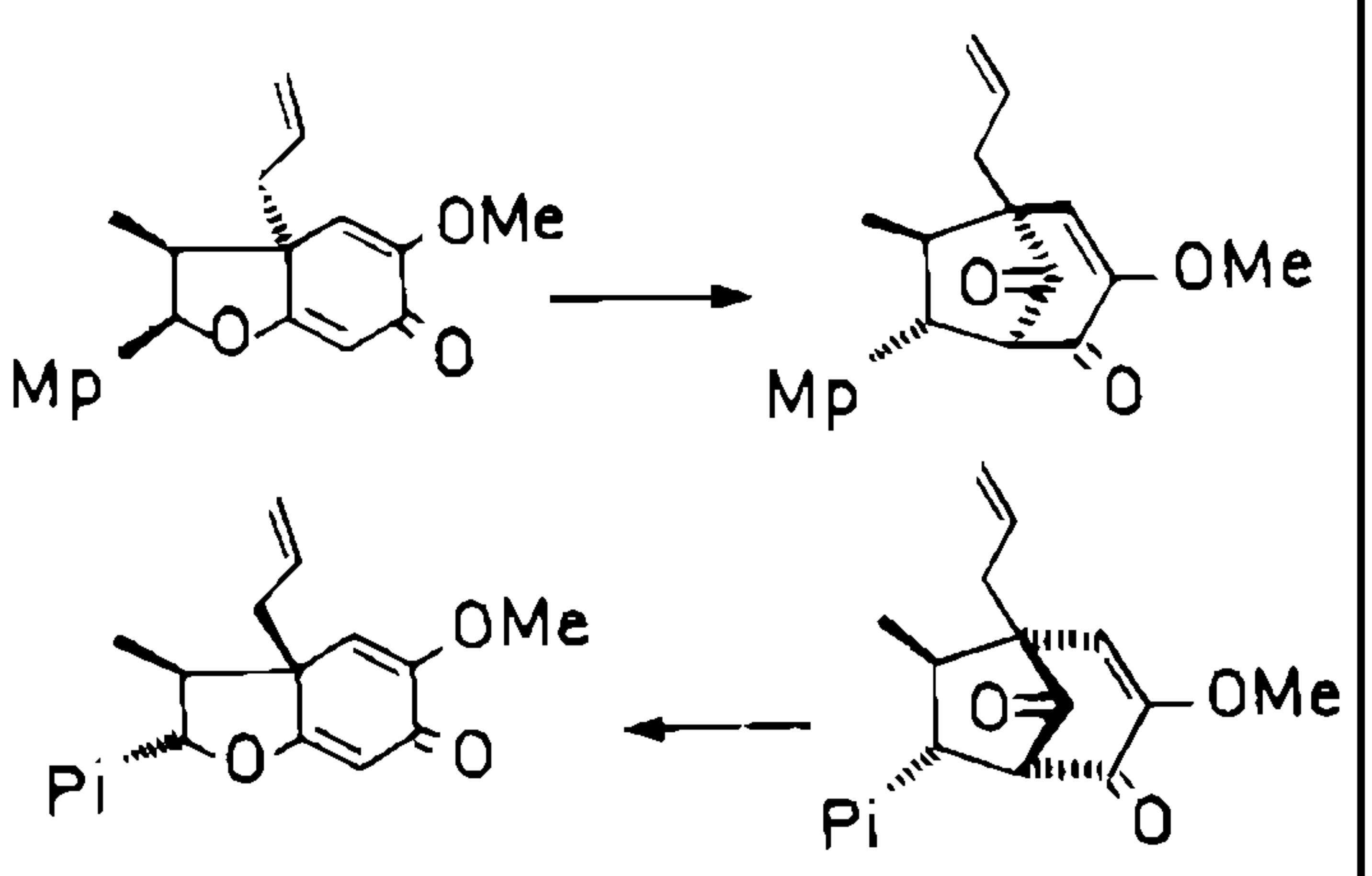
a Ar = Mp
b Ar = Tp

3

a Ar = Pi
b Ar = Mp

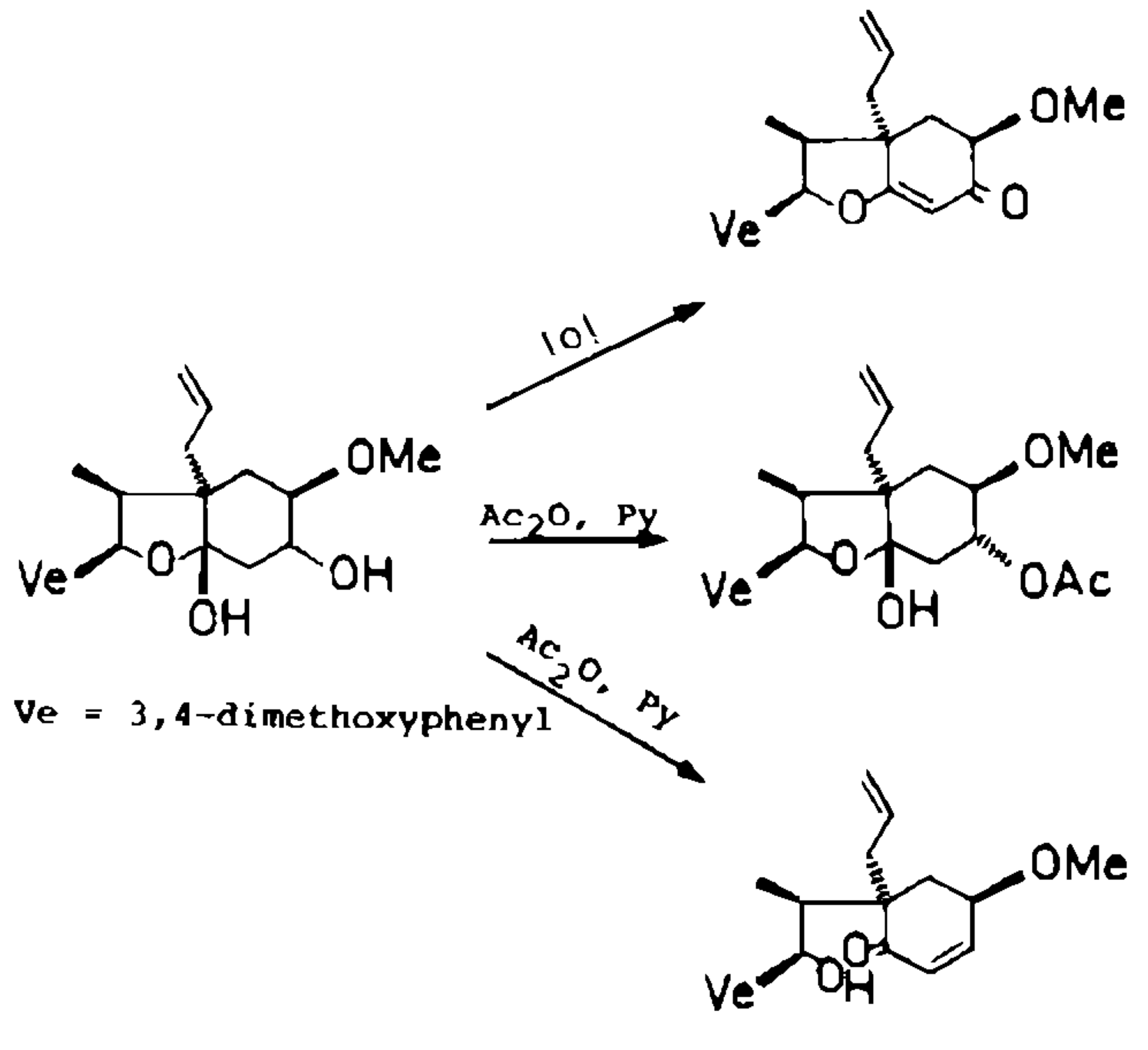
Pi = 3,4-methylenedioxyphenyl
Mp = 3-methoxy-4,5-methylenedioxyphenyl
Tp = 3,4,5-trimethoxyphenyl

Fig. 5: bicyclooctane neolignans from *Ocotea porosa*.



Pi = 3,4-methylenedioxyphenyl
Mp = 3-methoxy-4,5-methylenedioxyphenyl

Fig. 6: skeletal interconversion of neolignans.



Ve = 3,4-dimethoxyphenyl

Fig. 7: reactions of octahydrobenzofuran neolignans.

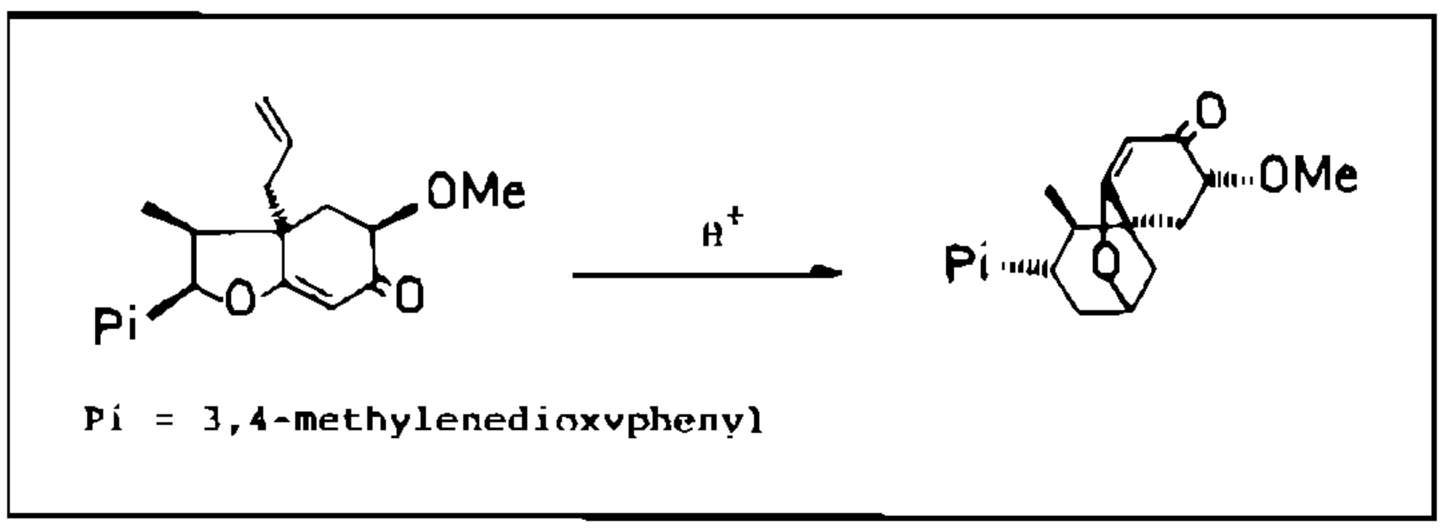


Fig. 8: rearrangements of porosin-B.

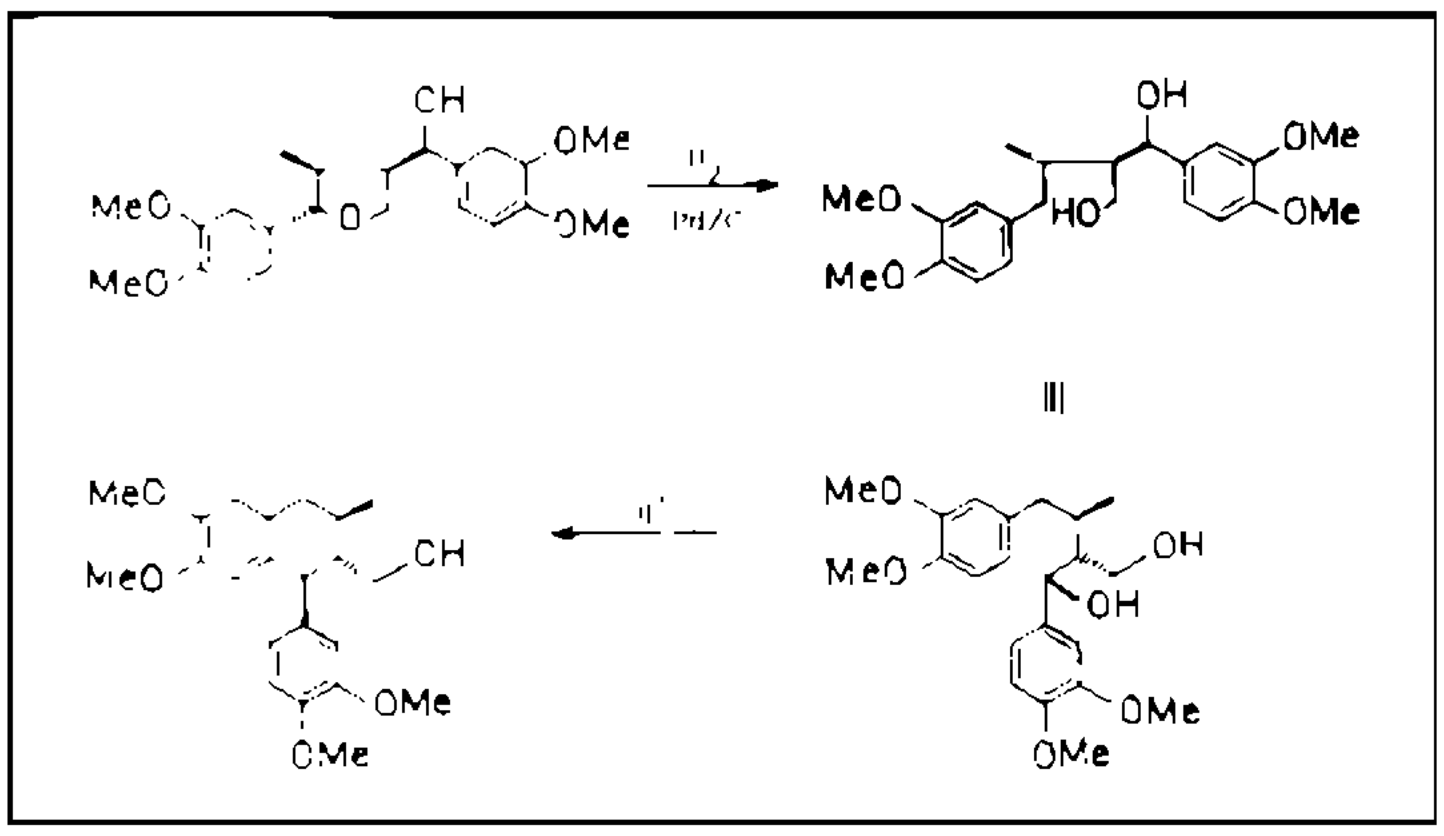


Fig. 9: transformation of magnostellin into aryltetralin neolignan.

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