ABSTRACT:
Cinnamon spice is derived from bark of several Castia and Cinnamomum genera. Depending on the origin, there are distinctive differences between composition of the water-soluble procyanidins, which are mainly consisting of A-type procyanidins, attributed with anti-diabetic activity. Trimers are dominant group, while tetramers are at ca. 20% of the trimner content and other oligomeric DPs contributing smaller pools. A Normal and Reverse Phase HPLC analysis of the bark of C. burmannii revealed a pattern of four trimers. The presence of cinnamtannin B-1 (1) and D-1 (2) have been previously documented. Two other trimers were isolated by the use of Centrifugal Partition Chromatography (Kromaton FCPC) followed by preparative HPLC and identified for the first time as aesculitannin B₃₄ (3) and lindetannin (4). All contain one A-type interflavan bond between top unit being epicatechin and the middle unit. Typically, some steric hindrance exists in these structures preventing free rotation around B-type bond producing different sets of signals detected by NMR, which complicates interpretation of the NMR spectra. The ratios of rotational isomers in 1-4 are different for each and are strongly solvent dependent. In methanol the ratios are equal to 1:3.7, 1:4.2, 1:4.5, and 1:91, while in DMSO they are equal to 1:1.4, 1:2.5, 1:9, and 1:7.5, respectively. These differences are explained using DFT optimization for different conformers showing two minima with energy barrier calculated from ¹H NMR temperature spectra as well as ¹³CNMR shielding constants and TD-DFT calculations.

Conclusions:
1. The rotamers ratio for the trimeric procyandins depends on the energy barrier between the two lowest-energy conformers (higher barrier – higher amount of the second conformer).
2. The barrier is a result of steric hindrances caused either by the aromatic rings (B, E or H) in case of trimers with ent-catechin as a middle unit (lindetannin, aesculitannin B) or by C3-OH hydroxyl group in case of the other trimers (cinnamtannin B-1 and D-1).
3. Aromatic ring hindrance is easier to overcome than C3-OH, since the location of the ring can be adjusted, whereas C3-OH hydroxyl group is bound in the pyran ring.

Literature:
1. KB Killday et al., J.Nat.Prod. (2011) 74, 1833

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