Nonpolar and medium polarity fractions from whole plant methanolic extracts of *Stevia monardifolia* afforded the new 7β-angeloyloxy-8α-isovaleroyloxylongipin-2-en-1-one 1 along with known 7β-8α-diangeloyloxylongipin-2-en-1-one 2 and 7β-8α-diangeloyloxylongipinan-1-one 3. Alkaline hydrolysis of a mixture of 1 and 2 gave 7β-8α-dihydroxylongipin-2-en-1-one 4 which was subjected to a single crystal X-ray diffraction study. The absolute configuration of the new compound 1, which is the third 7β-8α-dihydroxylongipin-2-en-1-one diester natural product isolated from a *Stevia* species, was fully characterized by one- and two-dimensional NMR spectroscopy and its absolute configuration was confirmed as the 4R,5S,7S,8S,10R,11R enantiomer from VCD studies in which the experimental spectra of the natural product and its acetylated derivative (5) were compared with the respective theoretical curves generated from the VCD frequencies calculated using DFT at the B3LYP/DGDZVP level of theory for the relevant conformers.