Sesquiterpenes, diterpenes, steroids and alkaloid from branches of *Xylopia brasiliensis* Spreng (Annonaceae)

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1. Subject and source

The branches of *Xylopia brasiliensis* (Annonaceae) were collected at the Instituto de Botânica, São Paulo – SP, Brazil on February 1998. A voucher specimen (number YOUNG10) has been deposited at the Herbarium of the Instituto de Botânica (SMA-SP).

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2. Previous works

The genus *Xylopia* belongs to the Annonaceae family, which comprises some 130 genera and 2300 species. Plants belonging to this genus have been described in several parts of the world, mainly in tropical regions of South and Central America, Africa and Asia (Hocquemiller et al., 1981; Takhtajan, 1986). Natural products of different classes such as acetogenins (Colman-Saizarbitoria et al., 1995), alkaloids (Hocquemiller et al., 1981; Harrigan et al., 1994; Moreira et al., 2003a), amides (Lajide et al., 1995), flavonoids (Anam, 1994; Moreira et al., 2003a), lignoids (Wahl et al., 1995) and terpenoids (Moraes and Roque, 1988; Moreira et al., 2003a,b) have been isolated. Besides these compounds, some studies have shown the occurrence of diterpene and sesquiterpene dimeric Diels-Alder adducts in branches of *Xylopia aromatica* (Martins et al., 1998, 1999) and *Xylopia amazonica* (Vilegas et al., 1991).

*X. brasiliensis* is a large tree distributed throughout Brazil and has been used in folk medicine, as a sedative and analgesic agent (Moreira et al., 2003b). Previous investigations of the chemical constitution of *X. brasiliensis* describe the occurrence of diterpenoids (Vilegas et al., 1989) and aporphine alkaloids (Casagrande and Merotti, 1970) from the fruits and stem bark, respectively. Antifungal aromadendrane sesquiterpene derivatives in the CH$_2$Cl$_2$ extract (Moreira et al., 2003b) and terpenoids (mono and sesquiterpenes) in the volatile oil (Lago et al., 2003), have been reported in the leaves of *X. brasiliensis*.

3. Present study

The dried and grounded branches of *X. brasiliensis* (1300 g) were extracted with CH$_2$Cl$_2$ at room temperature. The removal of the solvents in vacuum rendered 42.0 g of crude CH$_2$Cl$_2$ extract. Part of this extract (2 g) was subjected to CC on Si-gel, eluted with hexane/CH$_2$Cl$_2$/EtOAc/MeOH in gradient mixtures, to give seven fractions. Fraction 1 was purified by prep. TLC (CH$_2$Cl$_2$, twice) to give spathulenol (30 mg, Iwabushi et al., 1989) and *E*-phytol (10 mg, Rahman and Ahmad, 1992). Fraction 2 was subjected to purification over Si-gel column eluted with CH$_2$Cl$_2$:MeOH in gradient form to yield alismol (25 mg, Oshima et al., 1983), sitosterol + stigmasterol (30 mg, Ahmad et al., 1992), ent-16α,17-dihydroxy-kauran-19-oic acid (10 mg, Tanaka et al., 1985) and all-E-geranylgeraniol (23 mg, Coates et al., 1978; Jondiko and Pattenden, 1989). Fraction 3 was purified by prep. TLC (Si-gel, CH$_2$Cl$_2$:MeOH 95:5) to give ent-kaur-16-en-19-oic acid (12 mg, Hasan et al., 1982) and ent-16α,17-dihydroxy-kauran-19-oic acid (20 mg). Eudesm-4(15)-ene-1β,6α-diol (30 mg, Gonzalez et al., 1989) was isolated after CC on Si-gel eluted with CH$_2$Cl$_2$ followed by prep. TLC (CHCl$_3$, twice) of fraction 5. Fraction 6 was subjected to a Si-gel column eluted with CH$_2$Cl$_2$:MeOH in gradient form to yield a two subfractions. Subfraction 1 gave positive reaction with Dragendorff’s reagent, indicating the presence of an alkaloid and was purified by prep. TLC (CH$_2$Cl$_2$:MeOH 95:5, three times) to give O-methylmoschatoline (20 mg, Guinaudeau et al., 1983; Wijetatine et al., 1996). Subfraction 2 was subjected to prep. TLC
(CH$_2$Cl$_2$:MeOH 9:1, twice) to yield aromadendrane-4β,10α-diol (20 mg, Gijsen et al., 1992), aromadendrane-4α,10α-diol (10 mg, Goldsby and Burke, 1987) and alloaromadendrane-4α,10β-diol (15 mg, Goldsby and Burke, 1987). Fraction 7 was purified by Si-gel CC, eluted with CH$_2$Cl$_2$:MeOH in gradient form to yield sitosterol-3-O-β-D-glucopyranosyl (30 mg, Voutquenne et al., 1999). The structures of the known compounds were established by analysis of their physical and spectroscopic data (NMR and MS) and comparison with those reported in the literature.

4. Chemotaxonomic significance

Studies on the Xylopia genus deal mainly with acetogenins, terpenoids and alkaloids which show biological activity (Colman-Saizarbitoria et al., 1995; Fournier et al., 1994). This paper deals with the isolation of one alkaloid (O-methylmoschato-line) four diterpenoids (E-phytol, all-E-geranylgeraniol, ent-kaur-16-en-19-oic acid, ent-16α,17-dihydroxy-kauran-19-oic acid), six sesquiterpenes (spathulenol, alismol, eudesm-4(15)-ene-1β,6α-diol, aromadendrane-4β,10α-diol, aromadendrane-4α,10α-diol, alloaromadendrane-4α,10β-diol) and three steroids (sitosterol, stigmasterol, sitosterol-3-O-β-D-glucopyranosyl) from the branches of X. brasiliensis. The presence of all-E-geranylgeraniol has been described here for the first time in a Xylopia species while the compounds O-methylmoschato-line, alismol and eudesm-4(15)-ene-1β,6α-diol were not previously detected in X. brasiliensis but have been found only in Xylopia emarginata (Moreira et al., 2003a) and Xylopia championii (Wijetatine et al., 1996). The mention that the volatile oil from leaves of X. brasiliensis was composed mainly by spathulenol (40.8%), whose occurrence has been reported in all Xylopia species is important (Lago et al., 2003). In the branches and leaves of X. brasiliensis, this compound and several oxygenated related aromadendrane sesquiterpenes have also been found.

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References