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Alkaloid, flavonoids and terpenoids from leaves and fruits of *Xylopia emarginata* (Annonaceae)☆

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1. Subject and source

The leaves and fruits of *Xylopia emarginata* Mart. (Annonaceae) were collected in August, 1995 in Campo Grande, Mato Grosso do Sul State, Brazil. The plant was identified by Dr. Renato Mello Silva and a voucher specimen (number 101499) has been deposited at the Herbarium of the Instituto de Biociências — Universidade de São Paulo (SPF).

2. Previous works

Species of *Xylopia* (Annonaceae) have been shown to contain acetogenins (Colman-Saizarbitoria et al., 1995), alkaloids (Hocquemiller et al., 1981; Harrigan et al., 1994), flavonoids (Anam, 1994), terpenoids (Moraes and Roque, 1988), amides

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(Lajide et al., 1995), lignoids (Wahl et al., 1995), and dimer adducts formed by Diels–Alder reaction between sesquiterpene and diterpene derivatives (Martins et al., 1998; Martins et al., 1999). Two previous publications on the phytochemistry of *Xylopiá emarginata* have reported the presence of diterpenic dimers from stem bark (Vilegas et al., 1991) and sesquiterpenes from volatile oils from leaves and fruits (Brochini et al., 1999).

3. Present study

The powdered leaves (1100 g) and fruits (380 g) from *X. emarginata* were extracted with hexane and EtOH. The removal of the solvents rendered 12.5 g and 22.0 g of the hexane extracts and 111.0 g and 47.1 g of the EtOH extracts from leaves and fruits, respectively. The hexane extract from leaves was partitioned between MeOH:H₂O/hexane to give 10.1 g of the hexane and 2.0 g of the hydroalcoholic phases. The latter was submitted to CC and prep. TLC separations on Si-gel to give caryophyllene oxide (12 mg, Heymann et al., 1994), spathulenol (25 mg, Iwabuchi et al., 1989), alismol (12 mg, Oshima et al., 1983), *ent*-kaur-16-en-19-oic acid methyl ester (41 mg, Hasan et al., 1982), sitosterol + stigmaterol (5 mg, Ahmad et al., 1992) and 15-oxo-kaur-16-en-19-oic methyl ester (18 mg, Monte et al., 1988). The EtOH extract was partitioned between EtOAc and MeOH:H₂O 1:1 to give 31.1 g of the EtOAc phase and 80.0 g of the hydroalcoholic phase. The EtOAc phase was submitted to CC and prep. TLC separations on Si-gel to yield sitosterol-3-O-galactopyranoside (20 mg, Osman et al., 1975), quercetin-3-O-arabinofuranoside (15 mg; Markham et al., 1978) and quercetin-3-O-rhamnopyranoside (20 mg, Markham et al., 1978). The hexane extract from fruits was partitioned between hexane/MeOH:H₂O (95:5) to give 14.0 g of the hexane and 8.0 g of the hydroalcoholic phases. The latter was submitted to CC and prep. TLC separations on Si-gel to give caryophyllene oxide (10 mg, Heymann et al., 1994), spathulenol (20 mg, Iwabuchi et al., 1989), eudesm-4(15)-ene-1 β ,6 α -diol (15 mg, Gonzalez et al., 1989) and ruilopeziol (6 mg, Gonzalez et al., 1981). The EtOH extract from fruits was submitted to CC on Si-gel yielding sitosterol-3-O-galactopyranoside (15 mg, Osman et al., 1975), *ent*-16 α ,17-dihydroxy-kaurenoic acid (15 mg, Tanaka et al., 1985) and anonaine (15 mg, Guinaudeau et al., 1983). The structures of all these compounds were established by comparison of their physical and spectroscopic data (IR, NMR, MS) with those reported in the literature.

4. Chemotaxonomic significance

In the present work we isolated one alkaloid (anonaine), two flavonoids (quercetin-3-O-arabinofuranoside, quercetin-3-O-rhamnopyranoside), four sesquiterpenes (caryophyllene oxide, spathulenol, alismol, eudesm-4(15)-ene-1 β ,6 α -diol), four diterpenes (*ent*-kaurenoic acid, *ent*-15-oxo-kaur-16-en-19-oic acid, *ent*-16 α ,17-dihydroxy-kaurenoic acid and ruilopeziol) and three phytosterols (sitosterol, stigmaterol

and sitosterol-3-O-galactopyranoside). Several reports of genus *Xylopi*a have demonstrated the presence of alkaloids, flavonoids, terpenoids, steroids, etc., indicating that the isolated metabolites from *X. emarginata* are in agreement with the metabolic content of this genus. To our knowledge, this is the first time that quercetin-3-O-arabinofuranoside, quercetin-3-O-rhamnopyranoside, alismol and eudesm-4(15)-ene-1 β -6 α -diol have been described in *Xylopi*a. The sesquiterpene spathulenol can be defined as a taxonomic marker of this genus, because its occurrence has been described in all *Xylopi*a species. It is important to mention that diterpene and sesquiterpene Diels–Alder adducts were detected only in the stem bark of *X. aromatica* (Martins et al., 1998; Martins et al., 1999), *X. amazonica* and *X. emarginata* (Vilegas et al., 1991). The absence of these compounds in the leaves and fruits of *X. emarginata* suggests they may be organ specific.

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