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TRITERPENOIDS OF SAMBUCUS NIGRA AND S. CANADENSIS*

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Key Word Index—Sambucus nigra; S. canadensis; Caprifoliaceae; n-alkanes; palmitic acid; α - and β -amyrin; ursolic acid; oleanolic acid; sitosterol; stigmasterol; campesterol; quercetin; rutin.

The occurrence of triterpenoids in several Sambucus species has been reported [1–8]. It is of chemotaxonomic interest to examine triterpenoid components in the leaves of the following two elders.

Plant. Sambucus nigra. L., cultivated in Kyoto Herbal Garden, Takeda Chemical Industries, Ltd., Kyoto, Japan and S. canadensis L., cultivated in Botanical Garden, Faculty of Science, Osaka City University, Osaka, Japan.

Previous work. Ursolic acid and oleanolic acid from leaves [7] and α -amyrin, betulin, α -amyrone, ursolic acid and oleanolic acid from bark [2, 3] on triterpenoids of *S. nigra*. None on triterpenoids of *S. canadensis*.

Present work. The dried leaves of S. nigra and S. canadensis were separately extracted with MeOH. The MeOH extracts were concentrated respectively to syrup which was extracted successively with n-hexane, Et₂O and hot H₂O.

Constituents of S. nigra. The n-hexane extract was chromatographed on silica gel, affording a mixture of n-alkanes ($C_{2.5}$ – $C_{3.1}$), mp 64–66° (mainly n-nonacosane and n-hentriacontane, IR and GLC), colourless viscous liquid (A), and sitosterol, mp 141–142° (mmp, co-TLC and IR; ace-

tate, mp 125–127°, mmp, co-TLC and IR; containing small amount of stigmasterol and campesterol, GLC). A showed the properties similar to a mixture of α -amyrin and β -amyrin palmitates previously isolated from leaves of S. sieboldiana var. miquelli [8]. Hydrolysis of A gave a mixture, mp 182–184°, of α -amyrin and β -amyrin (7:3)(co-TLC, IR and GLC) and palmitic acid, mp 59–60° (mmp and IR; containing small amount of myristic, stearic and arachidic acids, GLC of methyl esters). The above data suggested A to be a mixture mainly of α -amyrin and β -amyrin palmitates.

The $\rm Et_2O$ extract was chromatographed on Si gel, yielding ursolic acid, mp 278–280° (mmp, co-TLC and IR; acetate, mp 277–279°, mmp, co-TLC and IR). The crude crystals of ursolic acid was found to contain oleanolic acid (GLC of its methyl ester).

The H₂O extract was chromatographed on polyamide and the MeOH eluate was rechromatographed on Si gel, affording quercetin, mp 307° (decomp.) (mmp, co-TLC, co-PPC, IR and UV) and rutin [9], mp 192° (decomp.)(mmp, co-TLC, co-PPC, IR and UV).

Constituents of S. canadensis. The following compounds were identified using chromatographic and identifiable methods similar to the case of S. nigra. A mixture of n-alkanes (C_{25} – C_{31} (mainly n-nonaconsane), colourless viscous

^{*} Part 3 in the series "Studies on the Constituents of Sambucus species." For Part 2 see Ref. [8].

Part* Oleanolic Ursolic Betulic Plant [Ref.] β -Amyrin Betulin acid acid 2-Amyrin 2-Amyrone acid S. canadensis L + L [5] {L [7] B [2, 3] S. chinensis + + + S. nigra + B [4] S. racemosa /L[1] + S. sieboldiana) W [6] + S. sieboldiana L[8] + + var. miguelii

Table 1. Distribution of triterpenoids in Sambucus species

liquid almost composed of α -amyrin and β -amyrin palmitates, and sitosterol containing small amount of stigmasterol and campesterol from the n-hexane extract; ursolic acid and oleanolic acid from the Et₂O extract; rutin [10] from the H₂O extract.

Comment. Distribution of triterpenoids in Sambucus species so far studied including present work, was shown in Table 1. It was indicated that α -amyrin and ursolic acid are widely distributed, accompanying often β -amyrin and oleanolic acid. In addition betulin seems to be present in bark and wood but not in leaves.

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^{*} L - leaves; B - bark; W - wood.