

COMPOSITAE

SANTONIN FROM *ARTEMISIA FRAGRANS*

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Key Word Index—*Artemisia fragrans*; Compositae; santonin.

Plant. *Artemisia fragrans* Willd. identified by Prof. A. Baytop, deposited in the Herbarium of Faculty of Pharmacy, University of Istanbul, Turkey, Voucher No. ISTE 22922: *Source.* Central Anatolia (Ankara).

According to the literature, there is a discrepancy about the presence of santonin in *Artemisia fragrans* Willd, Qazilbash has claimed the presence¹ and absence² of santonin and suggested³ that the variation was due to differing environmental conditions such as altitude, atmospheric humidity, soil humidity and so on. *Artemisia fragrans* was collected in late August from the Central Anatolia highlands (altitude 1000 m), with little atmospheric or soil humidity. 1 kg of the powdered dry plant was extracted with benzene giving 95 g of a green residue which was extracted with MeOH-*n*-hexane-H₂O (6:25:2). The solvent layers were separated and the lower aqueous layer extracted with CHCl₃. On evaporation yellowish crystals separated which gave 2 g of pure santonin, m.p. 169–170°, $[\alpha]_D^{20}$ –172° (c 2, CHCl₃) (IR, m. m.p. and TLC).

Extraction with MeOH, which was evaporated to dryness and re-extracted with 15% EtOH gave santonin in very poor yield.

¹ N. A. QAZILBASH, *Bull. Sci. Pharm.* **42**, 129 (1935); **29**, 7019 (1935).

² N. A. QAZILBASH, *Indian Pharmacist* **VI**, 3, 1, 65 (1950).

³ N. A. QAZILBASH, personal communication (1972).

ARTEVASIN: A NEW SESQUITERPENE LACTONE
FROM *ARTEMESIA TRIDENTATA**

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Key Word Index—*Artemesia tridentata*; Compositae; sesquiterpene lactone; artevasin.

Plant. *Artemesia tridentata* ssp. *vaseyana* (Rydb.) Beetle. Reported to be the most widely

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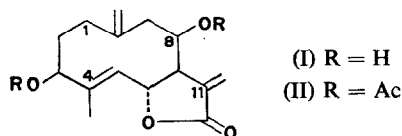
† R. O. ASPLUND and P. BALASUBRAMANIYAN, *Abstract of Papers, Am. Chem. Soc.* 158th Meeting (1969).

distributed of all the western sagebrushes.¹ Collection was made annually (1968–1971) in the Happy Jack Area, Albany County, Wyoming, U.S.A. (Rocky Mountain Herbarium voucher specimen No. 262 378). The non-woody aerial parts were collected.

Compound. Artevasin. M.p. 209–210° (corr.); $[\alpha]_D +244^\circ$ (c 0.75, EtOH); (Found: C, 68.21; H, 7.60%. $C_{15}H_{20}O_4$ requires: C, 68.16; H, 7.63%). $[\theta]_{258\text{ nm}} -3590$; UV, end absorption; ϵ 14 200 at 210 nm; IR, (KBr pellet), 3440 (OH), 1766 (α,β -unsaturated lactone), 1643 (exocyclic methylene), 1667 (double bond); MS, m/e 264 (M^+), 246 ($M-H_2O^+$), 231 ($M-H_2O-CH_3^+$), 228 ($M-2H_2O^+$), 91 (base peak); NMR, δ ppm in pyridine- d^5 , coupling constants J in Hz: 1.88 (d , 3H, J 1.0), vinyl methyl; 2.50 (m , 1H), C_7 ; 4.23 (t , 1H, J 9.0), C_6 ; 4.55 (m , 2H), C_3 , C_8 ; 4.87 (broad s , 1H) and 5.26 (broad s , 1H), C_{10} -methylene; 5.34 (d , 1H, J 3.0) and 6.18 (d , 1H, J 3.0), C_{11} -methylene; 5.45 (d , 1H, J 9.0), C_5 ; 5.40 (approx. broad s , 2H), OH. The last named peak which is obscured by other signals in this region disappears on addition of D_2O .

Artevasin is functionally isomeric with the three germacranolides, ridentin and tatridin-*A* and -*B* which have already been reported isolated from different sub-species of *A. tridentata*.^{2,3} It especially resembles ridentin in its spectral properties. The most certain evidence of its separate identity is its failure to give a definable color in the presence of HCl such as has been reported for ridentin and the tatridins. In these collections, artevasin is the most abundant sesquiterpene lactone being present in amounts as high as 0.3% of the total dry matter. In dried material, artevasin is either absent or present in very small amounts. In our hands, this compound has proved quite unstable; most chemical procedures yielding nothing but an apparently polymeric product.

Although the data presented here do not unequivocally establish the structure of artevasin, the near identity with ridentin and other structural features of the tatridins suggest that the most probable structure is (I). That is, the general structural features of ridentin with the OH group at C_8 rather than C_1 . The 1, 3 and 8 positions are the only sites of ring oxidation reported for lactones in this section of the genus.



Shafizadeh *et al.*⁴ have examined the sesquiterpene lactones of the Montana subspecies of *A. tridentata* and report they are eudesmanolides of the arbusculin type. They further report that such lactones were not found in equivalent Wyoming subspecies. The latter has been confirmed in part by our experience with Wyoming collections of *A. tridentata* spp. *vaseyana* in which we have found no evidence of eudesmanolides.

EXPERIMENTAL

Extraction. Coarsely chopped fresh leaves and soft stems (2.16 kg) were extracted 3 × MeOH at 25° for 36–48 hr each. The combined extracts were evaporated to 500 ml, and the syrup treated with 200 ml of

¹ A. A. BEETLE, *A Study of Sagebrush*, p. 54, University of Wyoming Agric. Expt. Stn. Bulletin, 368 (1960).

² M. A. IRWIN, K. H. LEE, R. F. SIMPSON and T. A. GEISSMAN, *Phytochem.* **8**, 2009 (1969).

³ M. A. IRWIN, Sesquiterpene Lactones of *Artemisia*. Ph.D. Dissertation, University of California, Los Angeles (1971).

⁴ F. SHAFIZADEH, N. R. BHADANE, M. S. MORRIS, R. G. KELSEY and S. N. KHANNA, *Phytochem.* **10**, 2745 (1971).

2.5% Pb(OAc)₂ and filtered. The filtrate was extracted 3 × CHCl₃ and the CHCl₃ evaporated to give an oil which was chromatographed over neutral Al₂O₃. The column was eluted with benzene followed by an Et₂O–MeOH gradient and the impure lactone obtained in 10% MeOH in Et₂O. The impure yellow lactone was treated with boiling EtOAc which on cooling yielded a white precipitate which was recrystallized from EtOH to obtain artevasin. Yield, 3.8 g.

Artevasin diacetate (II). The diacetate was prepared according to Irwin.³ It was not crystalline but was homogeneous to TLC and yielded a clear NMR spectrum. Principal points of difference with that of the parent compound were the disappearance of the broad singlet at δ 5.44 and the disappearance of the multiplet at δ 4.55 together with the appearance of signals at δ 4.18(1H) and δ 4.38(1H). The multiplicity of the latter signals could not be determined because of interference.

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TRITERPENOID AND STEROL CONSTITUENTS OF *BLAINVILLEA LATIFOLIA*

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Key Word Index—*Blainvillea latifolia*; Compositae; α -amyrin; β -amyrin; stigmasterol.

Plant. *Blainvillea latifolia* DC.¹ *Plant part.* Whole plant. *Source.* Chotanagpur, India. (Voucher specimen No. p-895 kept in the University of Kalyani). *Uses.* Not known. *Previous work.* None.

Whole plant. Extracted successively with petrol. (b.p. 60–80°) and benzene and the concentrated extracts of each chromatographed over Brockman 72 alumina separately. Petrol. and petrol.–benzene (7:3) eluates from both the chromatograms yielded an oily triterpenoid fraction. The benzene eluates afforded a colourless crystalline sterol identified as *stigmasterol* [m.p., m.m.p., IR, MS: m/e 412(M⁺), 369, 351, 314, 300, 271, 255]. The triterpenoid fraction was hydrolysed (10% alc.-KOH) and the semi solid thus obtained was chromatographed over alumina. A colourless crystalline solid, m.p. 159–160°, [426(M⁺), TLC-single spot] was obtained. Acetylation of this compound followed by fractional crystallization afforded two crystalline compounds, m.ps. 218–220° and 238–240°. The latter was characterized as *β -amyrin acetate* (m.p., m.m.p., IR; [α]_D) and the former as *α -amyrin acetate* (m.p., m.m.p., IR; [α]_D). Thus, the triterpenoid m.p. 159–160°, occurring in the original plant is a mixture of α - and β -amyrin.

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¹ D. PRAIN, *Bengal Plants, Botanical Survey of India* 1, 449 (1963).