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Tigogenin and Ursolic Acid from *Cestrum diurnum* Linn.

Leaves of *Cestrum diurnum* Linn. (Family, Solanaceae) were found to be rich in saponin. On extraction successively with petroleum ether (40°–60°), ether and 90% ethanol in a soxhlet, two products (A) and (B) were obtained from the ether and the ethanol fractions respectively. Product (A), $C_{30}H_{48}O_8$, m.p. 279–280°C, $[\alpha]_D^{24} + 62.7^\circ$ (pyridine), acetate m.p. 283–284°C, was identical with ursolic acid by comparison of mixed m.p. and IR-spectra with an authentic specimen.

Product (B), m.p. 269°C (decomp.), $[\alpha]_D^{23} - 48^\circ$ (pyridine), on hydrolysis with 5% hydrochloric acid gave a sugar fraction and a product (C), $C_{27}H_{44}O_3$, m.p. 207–208°C, $[\alpha]_D^{24} - 71^\circ$ (chloroform). The product (C) gave an acetate, $C_{29}H_{46}O_4$, m.p. 201–202°C, and a benzoate, $C_{34}H_{48}O_4$, m.p. 229–230°C, and was found to be tigogenin (IR-spectra compared). The sugar fraction on downward paper partition chromatography, using ethyl

acetate-pyridine-water (12:5:4) as eluent, showed the presence of xylose, glucose and galactose. The product (B) was found to be tigogenin^{1,2}.

Zusammenfassung. Aus *Cestrum diurnum* Linn. wurden Ursolsäure und Tigonin, $[\alpha]_D^{23} - 48^\circ$ (Pyridine) und aus Tigonin Tigogenin durch Hydrolyse isoliert bzw. erhalten.

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A Novel Oxidative Cyclization of 4-Arylthiosemicarbazides and Related Compounds

Thiosemicarbazide and 4-arylthiosemicarbazides are known¹⁻⁴ to undergo condensation with suitable reagents to afford different heterocyclic compounds. Likewise, thiosemicarbazones are also known to yield a variety of heterocyclic products either on condensation⁵⁻⁷ with or oxidation⁸⁻¹¹ by appropriate reagents. Oxidative cyclization of these materials, in general, result in 1, 3, 4-thiadiazoles, 4-aryl-1, 3, 4-thiadiazolines or 1, 2, 4-triazoles. A fusion to the aromatic ring borne on the 4-position of the thiosemicarbazide moiety in 4-arylthiosemicarbazides and the thiosemicarbazones, derived therefrom, has not been achieved hitherto by oxidative reactions, although references¹²⁻¹⁴ are available on the conversion of 1- or 4-phenylthiosemicarbazide to 2-aminobenzthiazole, in poor yields, by heating with concentrated HCl at 130°.

However, such an attack on the aromatic ring leading to the formation of a benzoheterocycle by the oxidation of an arylthiourea under HUGERSHOFF'S¹⁵ conditions is a common and well-exploited reaction for the synthesis of 2-amino- or 2-substituted amino benzthiazoles. In as much as 4-arylthiosemicarbazides can be considered as N-amino derivatives of N'-arylthioureas, it appeared to be of interest to study whether 4-arylthiosemicarbazides and the corresponding thiosemicarbazones obtained from a variety of aromatic aldehydes would undergo a similar cyclization by the action of bromine in chloroform.

We now report that 4-arylthiosemicarbazides undergo oxidative cyclization by bromine in chloroform to 2-hydrazino benzthiazoles (I) in fair yields (50–55%) (Table I, a). 4-Arylthiosemicarbazones of aromatic aldehydes, understandably, are more easily oxidizable under these

conditions to 1-arylidene 2-(2'-benzothiazolyl)hydrazines (II) in nearly quantitative yields (Table I, b). Both the sets of compounds have been authenticated by comparison with products prepared by unambiguous methods. The presence of some substituents in either the 4-aryl residue and/or the 1-arylidene moiety in the 4-arylthiosemicarbazones promotes an entirely different mode of cyclization to 3:4-diaryl-5-mercapto-1:2:4-triazoles (III).

The benzthiazolyl hydrazones (II) possess another site for cyclization and since it appeared desirable to achieve

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