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## A SAPOGENIN AND SUGARS FROM SAPONINS OF *OCTANDRA PHYTOLACCA*

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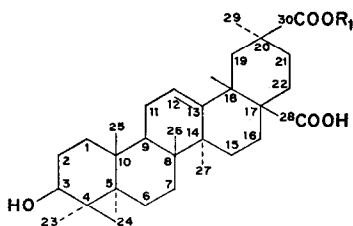
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**Key Word Index**—*Phytolacca octandra*; Phytolaccaceae; saponins; triterpenes; sugars.

**Source.** Wollongong and Paramatta districts N.S.W. Identified by Botany Dept., Botanical Gardens, Sydney, N.S.W.

The saponin content of *Phytolacca octandra* from the berries, leaves and root of the plant has been proved to yield a sapogenin which is identical with serjanic acid (the C<sub>30</sub> methyl ester of 3 $\beta$ -hydroxyolean-12-ene-28,30-dioic acid) (I).<sup>1</sup> The free acid, obtained on hydrolysis, is identical with spergulagenic acid (II).<sup>2-5</sup> Hydrolysis of the saponin also yielded rhamnose, mannose, glucose, fructose and glucuronic acid.



- (I) Serjanic acid      R<sub>1</sub> = Me  
(II) Spergulagenic acid      R<sub>1</sub> = H

Three new compounds have been prepared and examined, namely a bromo lactone of serjanic acid, a Jones' oxidation product of dimethyl spergulagenate and a heteroannular diene of dimethyl spergulagenate. The formation of a 12-bromo-13-28-lactone from the sapogenin showed that the free carboxyl group is attached to C<sub>17</sub> rather than C<sub>30</sub>. The ester group is at C<sub>30</sub> because the lithium aluminium hydride reduction product is a triol identical with that from spergulagenic acid and is queratarotriol. Oxidation of the hydroxyl group in the methylated sapogenin (dimethyl spergulagenate) by a Jones' oxidation yielded 3-keto derivative which gave a positive Zimmermann test and an ORD curve characteristic of C<sub>3</sub> amyrone ketones.<sup>6</sup> Selenium dioxide oxidation of the acetylated sapogenin yielded a heteroannular diene which gave a UV spectrum characteristic of  $\Delta^{11:12, 13:18}$  dienes of the oleanene series. Because I have not seen any physical data or spectra for free spergulagenic acid in published papers, the m.p., rotation and some spectral data are given in the Experimental.

<sup>1</sup> SAVOIR, R. and TURSCH, B. (1967) *Tetrahedron Letters* **23**, 2129.

<sup>2</sup> CHAKRABARTI, P., MUKHERJEE, D. K., BARUA, A. K. and DAS, B. C. (1968) *Tetrahedron* **24**, 1107.

<sup>3</sup> CHAKRABARTI, P., MUKHERJEE, D. K. and BARUA, A. K. (1966) *Tetrahedron* **22**, 1434.

<sup>4</sup> CHAKRABARTI, P. and BARUA, A. K. (1969) *J. Indian Chem. Soc.* **46**, 626.

<sup>5</sup> HARIHARAN, V. and RANGASWAMI, S. (1971) *Phytochemistry* **10**, 621.

<sup>6</sup> DJERASSI, C., OSIECKI, W., and CLOSSON, F. A. (1959) *J. Am. Chem. Soc.* **81**, 4587.

## EXPERIMENTAL

*Serjanic acid bromolactone* (III). M.p. 254° (Found: C, 62.4; H, 8.3; Br, 13.7% MW 579 (MS). Calc. for  $C_{31}H_{47}O_5Br$ : C, 64.2; H, 8.1; Br, 13.8%). The IR had a strong band at  $1770\text{ cm}^{-1}$  ( $\gamma$  lactone). MS  $m/e$  580 (17) 578 (16) 579, 562 (43) 560 (49) 561, 499 (M-80, 49), 291 (9.7) 246 (55), 207 (100).

*Jones' oxidation of the dimethyl ester spergulagenic acid*. The oxidation product (IV) m.p. 298° was crystallized from acetone. It gave a positive Zimmermann test and the ORD curve was a positive curve with a positive Cotton effect whereas the ORD curve of the dimethyl ester of spergulagenic acid was a positive plain curve with no Cotton effect. MS:  $m/e$  512 (Parent 44%) 452 (100), 306 (71), 256 (71), 233 (50), 205 (21) 187 (86). A chromium trioxide-pyridine oxidation gave the same oxidation product.

*Selenium dioxide oxidation of the acetyl dimethyl ester of spergulagenic acid* (V). Yielded from MeOH a white crystalline solid. M.p. 229–230°, MW 554 (MS). The UV shows absorption maxima at 242, 250 and 260 nm ( $\log \epsilon$  4.26, 4.32 and 4.13 respectively).

*Spergulagenic acid* (II). M.p. 320–322°,  $[\alpha]_D^{21} + 116$  (pyridine). Found C, 73.2; H, 9.5%, MW 486 (MS). Mass spec.  $m/e$  486 (6%), 468 (9), 453 (5), 440 (17), 425 (6), 330 (12), 278 (100), 232 (100), 207 (100), 187 (100). The IR had a broad absorption band at  $3525\text{ cm}^{-1}$  (OH) stretch, intense bands in the C–O stretching region  $1050$ ,  $1030$  and  $1000\text{ cm}^{-1}$  ( $3\beta$  equatorial OH) and  $1685\text{ cm}^{-1}$  (carboxyl). Since the acid was not sufficiently soluble in deuteriochloroform the NMR was run in pentadeuteropyridine and exhibited signals at  $\delta$  0.87, 0.73, 0.79, 0.80 (all 3H), 1.00 (6H), in all six tertiary methyl groups, 3.44 (OH), 5.68 (H at tri-substituted  $\Delta$ ).

*The sugars*. The sugars were identified by PC by running them against known sugars.

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## LA BORRERINE: NOUVEL ALCALOÏDE ISOLÉ DU *BORRERIA VERTICILLATA*\*

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**Key Word Index**—*Borreria verticillata*; Rubiaceae; indole alkaloids; borrerine; borreverine.

**Abstract**—*Borreria verticillata* has been found to contain two new tetrahydro- $\beta$ -carboline alkaloids, borrerine and an apparent dimer, borreverine. The structure of the former has been determined.

\* Partie XCIX dans la série "Alcaloïdes indolique". Pour partie XCVIII voir Ref 1.

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