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SYNTHESIS OF ERYTHROCENTAURIN SEMICARBAZONE

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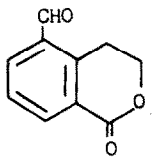
IN a previous communication,[1] we proposed the structure I for erythrocentaurin, which was produced by hydrolysis of swertiamarin with emulsin.[2] At that time, however, we could not exclude the structure II, as an alternative possibility. This communication describes the confirmation of the structure of erythrocentaurin by the synthesis of I, semicarbazone.

The course of the synthesis is illustrated in the following scheme: (V): $C_{11}H_{10}O_3$, m.p. 102-103°, (Found: C, 69.09; H, 5.48. Calc.: C, 69.46; H, 5.30) I.R. spectrum, 5.81, 5.91 . (VI): $C_{10}H_8O_3$, m.p. 225-226°, (Found: C, 68.04; H, 4.70. Calc.: C, 68.18; H, 4.58). (VII): $C_{10}H_8O_6$, m.p. 214-215°, (Found: C, 53.68; H, 4.02. Calc.: C, 53.58; H, 3.68) trimethylester, $C_{13}H_{14}O_6$, m.p. 108-109°, (Found: C, 58.49; H, 5.41. Calc.: C, 58.64; H, 5.30). (VIII): $C_{10}H_{14}O_3.H_2O$, m.p. 104-105°, (Found: C, 60.21; H, 8.31. Calc.: C, 59.98; H, 8.05), which is identical with the triol[1] from erythrocentaurin in I.R. spectrum and mixed m.p. (IX): $C_{10}H_8O_4$, m.p. 239-240°, (Found: C, 62.50; H, 4.52. Calc.: C, 62.50; H, 4.20), which is identical with the lactone carboxylic acid[1] from erythrocentaurin in I.R. spectrum and mixed m.p. (XI): (semicarbazone of I), m.p. 218-219°, whose

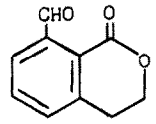
[1] T. Kubota and Y. Tomita, Chem. & Ind. 230 (1958).

[2] T. Kariyone et al., J. Pharm. Soc. Japan 47, 133 (1927); 49, 702 (1929).

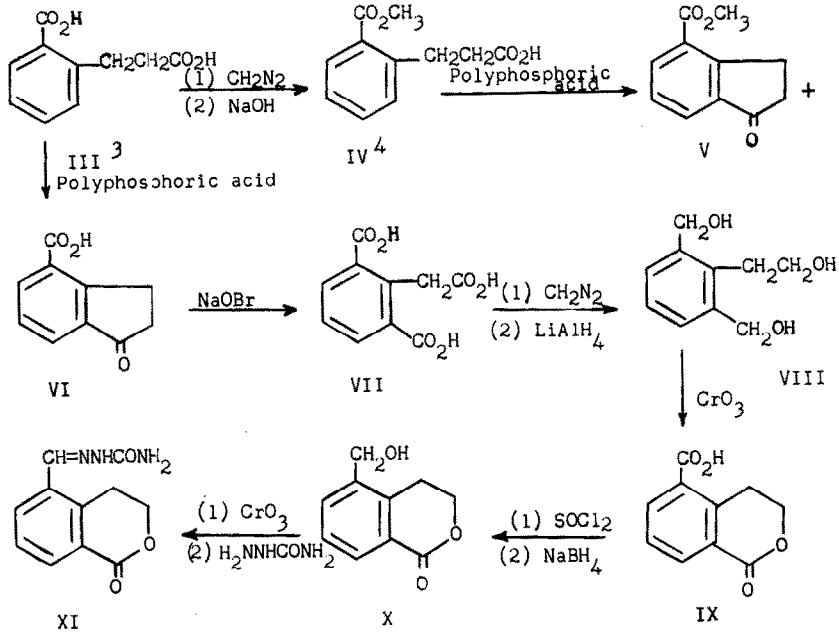
mixed m.p. and I.R. spectrum showed the identity of (XI) with the semicarbazone of natural erythrocentaurin (I).



I



II



The alternative lactone formula IXa of the reaction product of the triol VIII was eliminated by the following evidence (I) Methylation of XVI followed by lithium aluminum hydride reduction yielded XVII which, on chromic

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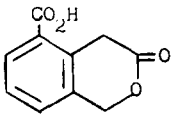
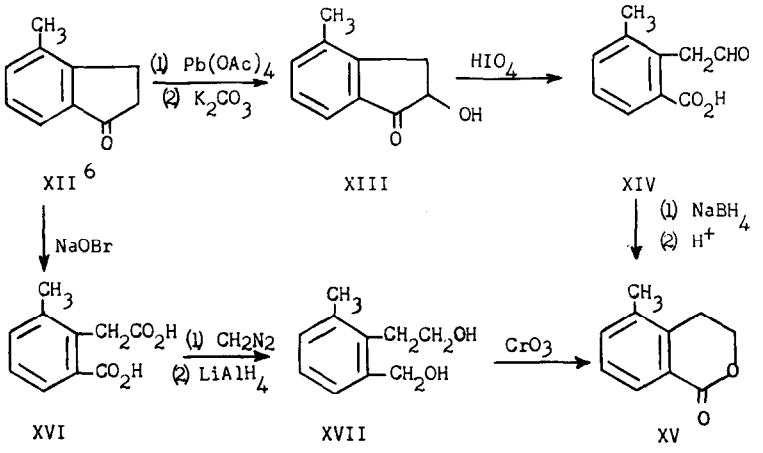
[3] Organic Syntheses 34, 8 (1954)

[4] S. Murahashi and R. Anzai, Chem. High Polymers 3, 33 (1946).

acid oxidation, gave the lactone XV, analogous to the lactone IX, whose structure was confirmed by a sequence of reactions, XII to XV. (2) The infra-red band (5.82μ) of IX is in agreement with the structure of an aryl-conjugated δ-lactone, such as gentinine (5.82μ)[5] and XV (5.87μ). (XIII): $C_{10}H_{10}O_2$, m.p. 109-110° (Found: C, 74.56; H, 6.22. Calc.: C, 74.05; H, 6.22). (XIV): $C_{10}H_{10}O_3$, m.p. 151-152° (Found: 67.46; H, 5.68. Calc.: C, 67.40; H, 5.66) (XV): $C_{10}H_{10}O_2$, m.p. 72-73° (Found: 74.25; H, 6.36. Calc.: 74.05; H, 6.22). (XVI): $C_{10}H_{10}O_4$, m.p. 184-185° (Found: C, 61.76; H, 5.22 Calc.: 61.85; H, 5.19).



IXa



[5] T.R. Govindachari et al., J.Chem.Soc. 551 (1957).

[6] R.N. Chakravarti, J. Indian Chem.Soc. 20, 393 (1943).