Tetrahedron Letters No. 27, pp 2283 - 2286, 1975. Pergamon Press. Printed in Great Britain.

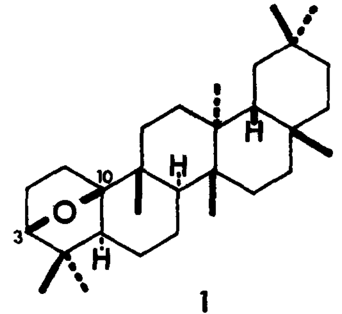
THE SYNTHESIS OF DENDROPANOXIDE FROM FRIEDELIN

Takahiro Torii, Kazuo Tachibana, Sachiko Yamada,
Takahiko Tsuyuki, and Takeyoshi Takahashi
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo, Japan

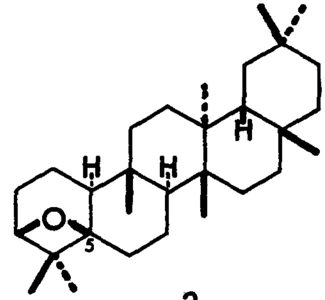
(Received in Japan 23 April 1975; received in UK for publication 19 May 1975)

Different names, that is, dendropanoxide,1) epoxyglutinane,2) and campanulin,3) have been given to a triterpene oxide, $C_{30}H_{50}O$, isolated from a number of plants of the families Araliaceae and Ericaceae.4) Two alternative structures, D:B-friedo-olean-3,10-oxide (1)2,3,5) and D:B-friedo-olean-3,5-oxide (2),1,2,4) have been proposed for the triterpene. Finally, the structure of this triterpene oxide (dendropanoxide6); epoxyglutinane ; campanulin) has recently been determined to be D:B-friedo-olean-3β,10β-oxide (1) by X-ray study.7) Dendropanoxide (1) and friedelin (3)8) are triterpenes closely related each other in view of biogenetic considerations. We now describe the conversion of friedelin (3) into dendropanoxide (1).

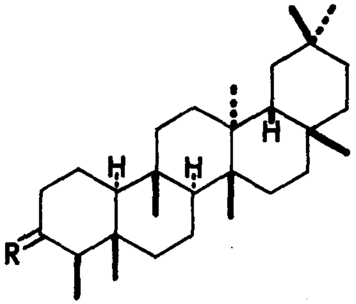
Friedelin (3) was converted *via* friedelan-3β-ol (4)8a,b,9) into friedel-3-ene (5)8a,b) by the known procedures. Epoxidation of 5 with m-chloroperbenzoic acid gave 3α,4α-epoxyfriedelane (6)10) and 3β,4β-epoxyfriedelane (7), m.p. 202-204°, M^+ at m/e 426 ($C_{30}H_{50}O$); PMR ($CDCl_3$): δ 2.95 (1H, br., $W_{1/2}$ 6 Hz; $C_{(3)}$-H), in a ratio of about 2 : 1. The β-epoxide (7 ; 300 mg) in ether was treated with BF_3-Et_2O at - 10° until a complete disappearance of the starting material (30 min) to give a mixture showing four spots on silica gel TLC impregnated with silver nitrate. The least polar material was separated by silica gel column chromatography impregnated with silver nitrate to afford an oxide (1 ; 65 mg), m.p. 206-208°, $[\alpha]_D$ + 71° ($CHCl_3$; c, 1.0), M^+ at m/e 426 ($C_{30}H_{50}O$); PMR ($CDCl_3$): δ 3.75 (1H, d, J = 5 Hz; $C_{(3)}$-H), which was found to be identical (m.p., mixed m.p., $[\alpha]_D$, IR, PMR, mass spectrum and TLC) with dendropanoxide



1

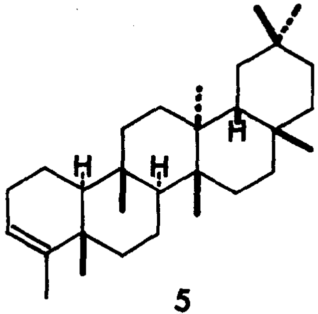


2

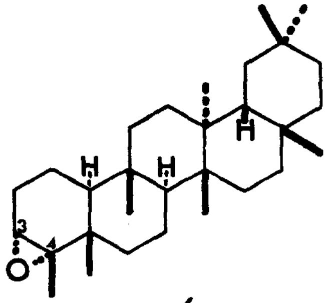


3 R = O

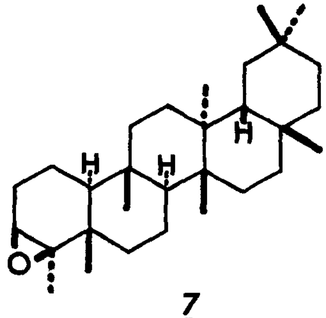
4 R = β-OH, α-H



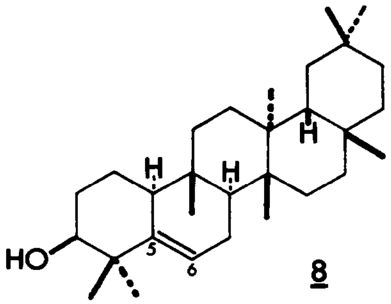
5



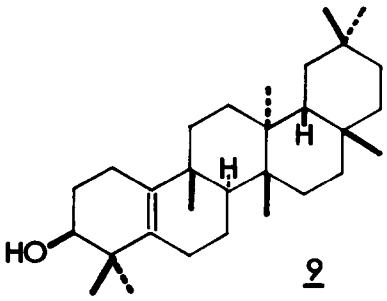
6



7



8



9

(1)1,6,11) and with D:B-friedo-olean-3β,10β-oxide (1) isolated from Rhododendron macrophyllum by Block and Constantine.4,5)

The most polar product (41 mg) was identified to be D:B-friedo-olean-5-en-3β-ol (8).4,5) The second polar product (64 mg) was purified by recrystallization and identified to be D:B-friedo-olean-5(10)-en-3β-ol (9).4,5) Identification of the fourth product is under way.

A mechanism involving a non-concerted process can account for the formation of 1 from the β-epoxide (7). A treatment of the α-epoxide (6) with $SnCl_4$10a) or with BF_3-Et_2O10b) was reported to give D:B-friedo-olean-5(10)-en-3α-ol,10) olean-12-en-3α-ol,10b) 18-iso-olean-12-en-3α-ol,10b) olean-13(18)-en-3α-ol,10b) and 18-iso-A-neo-oleana-3(5),12-diene;10b) no ether was reported to be formed in these cases.10)

Acknowledgement : We wish to thank Professor John H. Block and Professor George H. Constantine, Jr., Oregon State University, for a generous gift of an authentic sample of D:B-friedo-olean-3β,10β-oxide.

REFERENCES

1) K. Kimura, Y. Hashimoto, and I. Agata, Chem. Pharm. Bull. (Tokyo), **8**, 1145 (1960).

2) H. R. Arthur and W. H. Hui, J. Chem. Soc., 1961, 551.

3) S. Rangaswami and K. Sambamurthy, Proc. Indian Acad. Sci., **54A**, 132 (1961).

4) G. H. Constantine, Jr. and J. H. Block, Phytochemistry, 9, 1659 (1970). And the references cited therein.

5) J. H. Block and G. H. Constantine, Jr., Phytochemistry, 11, 3279 (1972).

6) In the present paper, the name "dendropanoxide" was used for this triterpene oxide.

7) J. D. White, J. Fayos, and J. Clardy, J. Chem. Soc. Chem. Comm., 1973, 357.

8) a- E. J. Corey and J. J. Ursprung, J. Amer. Chem. Soc., 78, 5041 (1956). b- G. Brownlie, F. S. Spring, R. Stevenson, and W. S. Strachan, J. Chem. Soc., 1956, 2419. c- T. Takahashi and G. Ourisson, Bull. Soc. Chim. France, 1956, 353. d- H. Dulter, O. Jeger, and L. Ruzicka, Helv. Chim. Acta, 38, 1268 (1955).

9) a- T. Brunn, Acta Chem. Scand., 8, 71 (1954). b- P. R. Jefferies, J. Chem. Soc., 1954, 473.

10) a- J. W. ApSimon, R. R. King, and J. J. Rosenfeld, Can. J. Chem., 47, 1989 (1969). b- P. Sengupta, B. Roy, S. Chakraborty, J. Mukherjee, and K. G. Das, Indian J. Chem., 11, 1249 (1973).

11) An authentic sample of dendropanoxide was obtained by isolation from Dendropanax trifidus Makino following the procedures described in ref. 1.