Tetrahedron Letters No. 17, pp. 1127-1130, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE STRUCTURE OF ARBORESCIN

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(Received 15 April 1963)

THE guaianolide arborescin was isolated by Meisels and Weizmann[1] from Artemisia arborescens (Compositae), a plant used for contraceptive purposes by the ancient Greeks and Arabs.[2] Mazur and Meisels[3] proposed the structure I, which was questioned by de Mayo.[4] Later,[5] this lactone was found to occur along with globicin (IIIb[6]) in Matricaria globifera (Thunb.) Druce (Compositae), and, after further experiments with arborescin, the alternative structure II was favored for it.[7] These

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[1] A. Meisels and A. Weizmann, J. Am. Chem. Soc., 75, 3865 (1953).

[2] W. Jöchle, Ang. Chem., International Edition, I, 541 (1962).

[3] Y. Mazur and A. Meisels, Chem. and Ind., 492 (1956).

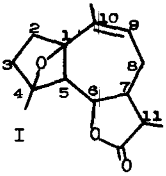
[4] P. de Mayo, Perfumery and Essential Oil Record, 48, 71 (1957).

[5] Z. Čekan, V. Procházka, V. Herout, and F. Šorm, Coll. Czech. Chem. Comm., 25, 2553 (1960).

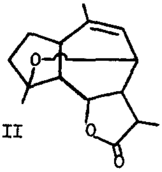
[6] R. B. Bates, V. Procházka, and Z. Čekan, Tetrahedron Letters, in press; V. Procházka, Z. Čekan, and R. B. Bates, Coll. Czech. Chem. Comm., in press.

[7] Z. Čekan and V. Procházka, 2nd International Symposium on the Chemistry of Natural Products, Prague, 1962.

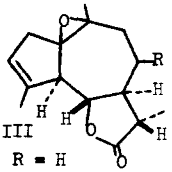
experiments included a chemical correlation with artabsin, for which structure IV had been proposed:[8a] tetrahydroartabsins b and c were among the products of the hydrogenolysis of arborescin in acetic acid with a platinum catalyst. Thus, the location of one end of the oxide bridge in arborescin at C_4 seemed firmly established. However, further results which we now wish to report indicate the structure of arborescin to be IIIa.



I

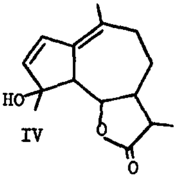


II

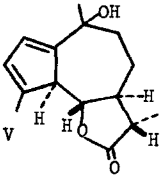


III

a R = H
b R = OAc



IV



V

It has recently been established[8b] that artabsin has the structure V rather than IV, indicating that one of the points of attachment of the oxide bridge in arborescin is at C_{10} and thus ruling out both proposed structures. In addition, the NMR (Figure 1) and NMDR spectra of arborescin are incompatible with these structures, since the proton absorbing at 5.98 τ, which from its chemical shift must be the proton at C_8, is strongly coupled (10 cps) with a proton absorbing at 7.18 τ which from its chemical shift must be allylic.

The structure IIIa (with the exception of the configuration of the methyl at C_{11}) can be derived as follows. Dehydrogenation studies of

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[8a] V. Herout, L. Dolejš, and F. Šorm, Coll. Czech. Chem. Comm. 22, 1914 (1957).
[8b] M. Suchý, V. Herout, and F. Šorm, ibid in press.

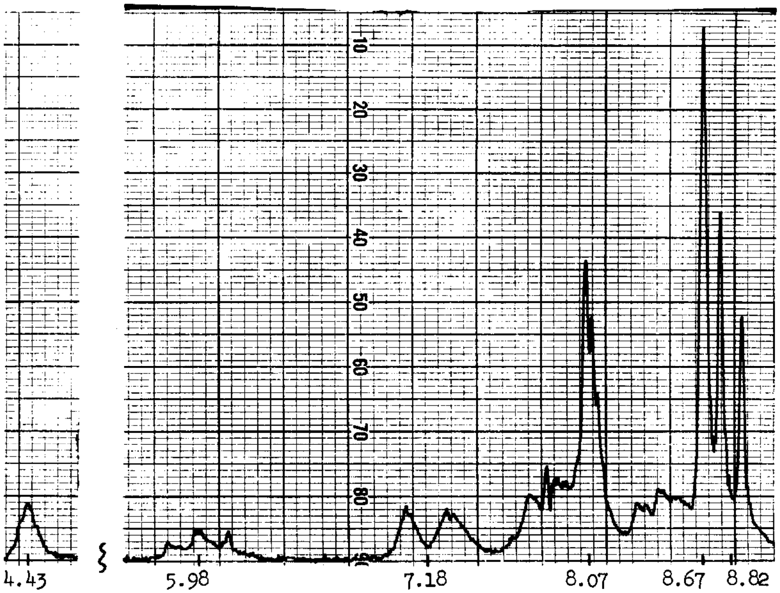

Figure 1. NMR spectrum of arborescin at 60 Mc. in $DCCl_3$, with chemical shifts in τ units

arborescin and its derivatives leads to a variety of azulenes, showing the carbon skeleton and the location of the γ-lactone ring.[1,3] The ether and double bond groupings can then be located as shown from the NMR and NMDR results. The spectra show one vinyl proton (at 4.43 τ) and one vinyl methyl (at 8.07 τ; coupling constant with the vinyl proton, 2 cps), and thus there must be either a 3,4 or a 9,10 double bond. The absorption at 5.98 τ must be due to a proton at C_6 (no satisfactory structures with it elsewhere can be written), and since, as noted above, this proton is strongly coupled with an allylic proton, the double bond must be in the 3,4 position. Due to the lack of absorption in the 4.5-6.9 τ region other than that for the C_6 proton, the ether must be ditertiary, and must involve the 1 and 10 positions, since the alternative positions, 5, 6, 7, and 11, must bear hydrogens to fit the splitting patterns for the proton at C_6 and the methyl at C_{11}. The stereochemical arguments are identical with those given for globicin,[8] with the exception that the C_7-C_{11} coupling constant could not be determined for arborescin and thus the configuration at this location can not be deduced from NMR evidence.

The revised structure for artabsin (V) coupled with the chemical correlation of artabsin with arborescin mentioned above serve to confirm most of the above structural features, and in addition allow the assignment of the configuration shown for the C_{11} methyl group.

Thus, although no chemical correlation has been made between globicin and arborescin, it appears that arborescin possesses the desacetylglobicin structure IIIa[9,10].

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[9] The correctness of formula IIIa has now been synthetically verified (M. Suchý, V. Herout, and F. Šorm, ibid., in press).

[10] This work was supported in part by the U. S. Public Health Service.