

THE STRUCTURE OF ALBENE, A HYDROCARBON
FROM THE PLANTS OF THE GENERA PETASITES AND ADENOSTYLES

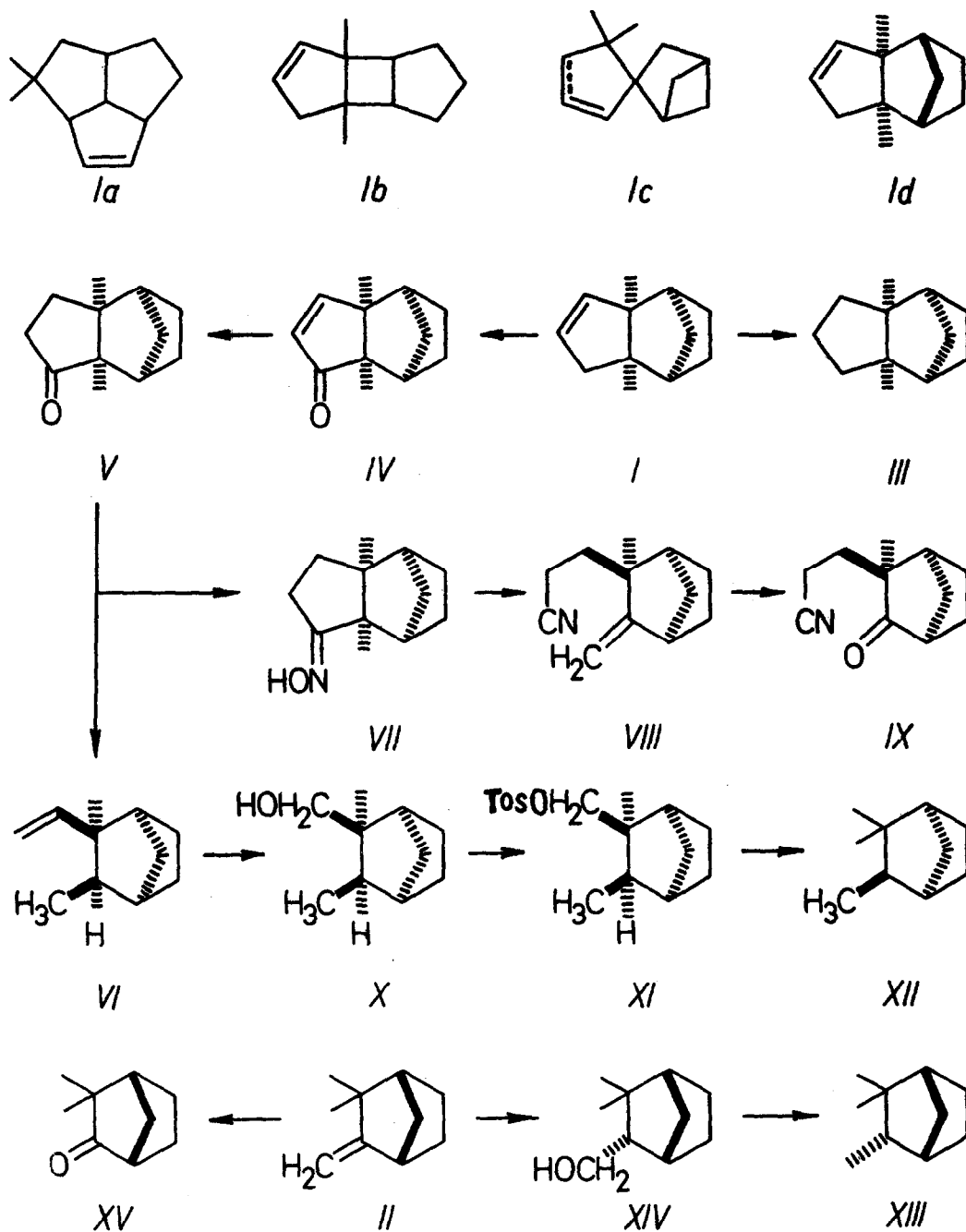
K. Vokáč, Z. Samek, V. Herout and F. Šorm
Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences, Prague

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Several years ago Novotný and co-workers¹ isolated from *Petasites albus* (L.) Gearth a crystalline hydrocarbon of the composition $C_{12}H_{18}$ to which they gave the name albene (I). Later on it was found that the occurrence of albene is a common feature of the genera *Petasites* and *Adenostyles*^{2,3}. In the first structural studies it was shown that albene is a tricyclic hydrocarbon with a disubstituted double bond in a five-membered ring, and the structure Ia was proposed provisionally⁴. Presently we returned to the completion of the structural study of albene and using spectral methods and direct correlation with (+)-camphene (II) we proved⁵ that albene has the structure I.

We isolated albene newly from the hydrocarbon fraction of the plant extract by chromatography on silica gel impregnated with silver borate. The hydrocarbon obtained had m.p. 110-115°C and $[\alpha]_D^{20} -9.2^\circ$ (c 0.54, $CHCl_3$). Its p.m.r. spectrum (100 MHz, $CDCl_3$) exhibited signals of two tertiary methyl groups (δ 0.95, s, 6H) and of a fragment $C^x-CH_2(a)-CH(b)=CH(c)-C^x$ (C^x - tetrasubst. sp^3 -C-atom) in a five-membered ring (A) ($2H_a$: δ 2.23, t; $|J_{a,b} + J_{a,c}| = 4.4$ Hz; H_b, H_c : dt, δ 5.26 and 5.56, $J_{b,c} = -5.5$ Hz), and ruled out structure Ia directly. The structure of the five-membered ring A was also corroborated by the presence of signals corresponding to the protons of the fragment $C^x-CH_2-CH(X)-CH(X)-C^x$ found in the p.m.r. spectra of a series of simple derivatives⁵, e.g. with X = Br or OH. Furthermore, these p.m.r. spectra also indicated the presence of two isolated methine groups $-CH$ in the albene molecule⁶. Albene formed dihydroderivative III (m.p. 125-130°C) which according to its $[\alpha]_D^{20} \pm 0^\circ$ (c 0.62, $CHCl_3$) and $[\phi]_{230-400} \pm 0^\circ$ (c 0.121, cyclohexane, 26°C) as well as to its p.m.r. spectrum should possess inner symmetry. No characteristic signals of cyclopropane protons were found in the p.m.r. spectra of albene or its derivatives. The presence or absence of gem. dimethyl group could not be derived unambiguously from the i.r. spectra.

Considering all these aspects and the tricyclic nature of the albene skeleton the set of the possible structural formulas was reduced to three groups of probable alternatives I, Ib and Ic. The structure I was then selected in the following manner (cf. scheme)⁵.



On oxidation⁷ of albene (K_2CrO_4 /acetic anhydride + acetic acid, 40°C) we obtained α,β -unsaturated ketone IV (m.p. 125-135°C, λ_{max} 227 nm, $\log \epsilon$ 3.91) which on hydrogenation (Pd-SrCO₃/ethanol) gave saturated ketone V (m.p. 146-150°C, ν (C=O) 1712 cm⁻¹). By photolysis of V (hexane, 60°C) we obtained liquid olefin VI (isolated by chromatography on silica gel impregnated with silver borate) the p.m.r. spectrum of which indicated the presence of one tertiary and one secondary methyl groups and of a vinyl group CH₂=CH-C^x. Ketone V was also transformed to oxime VII (m.p. 108-111°C) in the usual manner. The latter gave unsaturated nitrile VIII (m/e 175, ν (C≡N) 2250 cm⁻¹) on reaction with PCl₅⁸ (ether + benzene, 20°C). The p.m.r. spectrum of VIII indicated the presence of one tertiary methyl and one exomethylene groups. The formation of compounds VI and VIII excluded the alternatives Ic. By ozonisation⁹ of VIII (CH₂Cl₂/pyridine, -78°C) we obtained ketonitrile IX (b.p. 120°C/12 mm Hg, ν (C≡N) 2249 and ν (C=O) 1741 cm⁻¹) the i.r. spectrum of which indicated the presence of a cyclopentanone ring and excluded therefore the alternative Ib.

The correctness of the structure I for albene was then corroborated by direct correlation with (+)-camphene (II) (cf. scheme). Ozonisation of VI and reductive decomposition of ozonides with LAH gave alcohol X (m.p. 64-72°C). Its tosylate XI (m.p. 65-67.5°C) on reduction with LAH in ether gave a hydrocarbon XII (obtained in liquid form; $[\alpha]_D^{20}$ -0.5°, c 0.43, CHCl₃), identical according to its p.m.r. and i.r. spectra with endo-camphane XIII¹⁰ (m.p. 69-70°C; $[\alpha]_D^{20}$ -3.7°, c 0.55, CHCl₃) prepared from (+)-camphene (II) via the endo-camphanol XIV¹¹.

The stereochemistry of albene (I) was deduced in the following manner. The inner symmetry of dihydroalbene III indicated cis-fusion of A and B rings, and hence also four possible stereostructures formed by two enantiomeric pairs of I and Id. The differentiation between these possibilities was carried out directly by comparison of the ORD curves of ketonitrile IX and camphenilone XV¹² which we prepared by ozonisation⁹ of (+)-camphene (II). The ORD curve of IX displayed a negative CE at 286 nm with amplitude a -258 (c 0.226, methanol, 26°C) and the ORD curve of XV had a positive CE at 280 nm with a +380 (c 0.775, methanol, 26°C). It can be assumed that the contribution of the cyanoethyl group affects the amplitude of CE only, and that the hypothetical mirror-image isomer of IX with a +258 corresponding to camphenilone (XV) should thus have the cyanoethyl group in the negative octant; hence, the ketonitrile IX has the enantiomeric stereostructure IX, while albene has the relative and absolute stereostructure I. The proof of the enantiomeric nature of XII and XIII based on the ORD plain-curves measurements, was unsuccessful until now due to small amount and low purity of XII⁵.

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