Tetrahedron Letters No.11, pp. 1401-1404, 1968. Pergamon Press. Printed in Great Britain.

The Structure of Kablicin, the Main Component of the Light Petroleum Extracts of Petasites kablikianus TAUSCH.ex BERCHT. and of Petasites paradoxus (RETZ)BAUMG. Rhizomes

L.Novotný, Z.Samek, V.Herout and F.Šorm
Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Science, Prague

(Received in UK 17 November 1967)

In a review article on the components of some Petasites species[1] and in the communication concerning the chemotaxonomy of certain European Petasites species[2] the isolation of kablicin I has been reported; kablicin is the main and typical component of the light petroleum extract of Petasites kablikianus rhizomes. We have now found[3] that Petasites paradoxus contains the same substances as P. kablikianus. This represents evidence that both species have the same hybridogenic origin from the same parental species, Petasites hybridus GAERTN., MEY. et SCHERB., and Petasites albus GAERTN.

Kablicin is a poorly crystalline compound melting at 72°C, $C_{25}H_{34}O_6$ (mass number 430), $[\alpha]_D^{20}$ - 18.4°, λ_{max}^{EtOH} 223 nm, log ε 4.19, $\nu_{max}^{CHCl_3}$ 3590, 1700, 1642, 1562 cm^{-1}. Its infrared spectrum and other properties led us to the conclusion that kablicin is a furoeremophilane derivative. In accordance with this consideration its PMR spectrum (100 MHz, $CDCl_3$) showed characteristic signals due to the α-furan proton (1 H; 7.14 ppm) and to the methyl group in the β-position of the furan nucleus (1.84 ppm; the signal is split by the α-proton and is covered by the signals of methyls of the ester groups, the interaction was proved by decoupling experiments), of one tertiary methyl group (3 H; 1.10 ppm) and of one secondary methyl group (3 H; doublet, 0.90 ppm, J = 7 Hz).

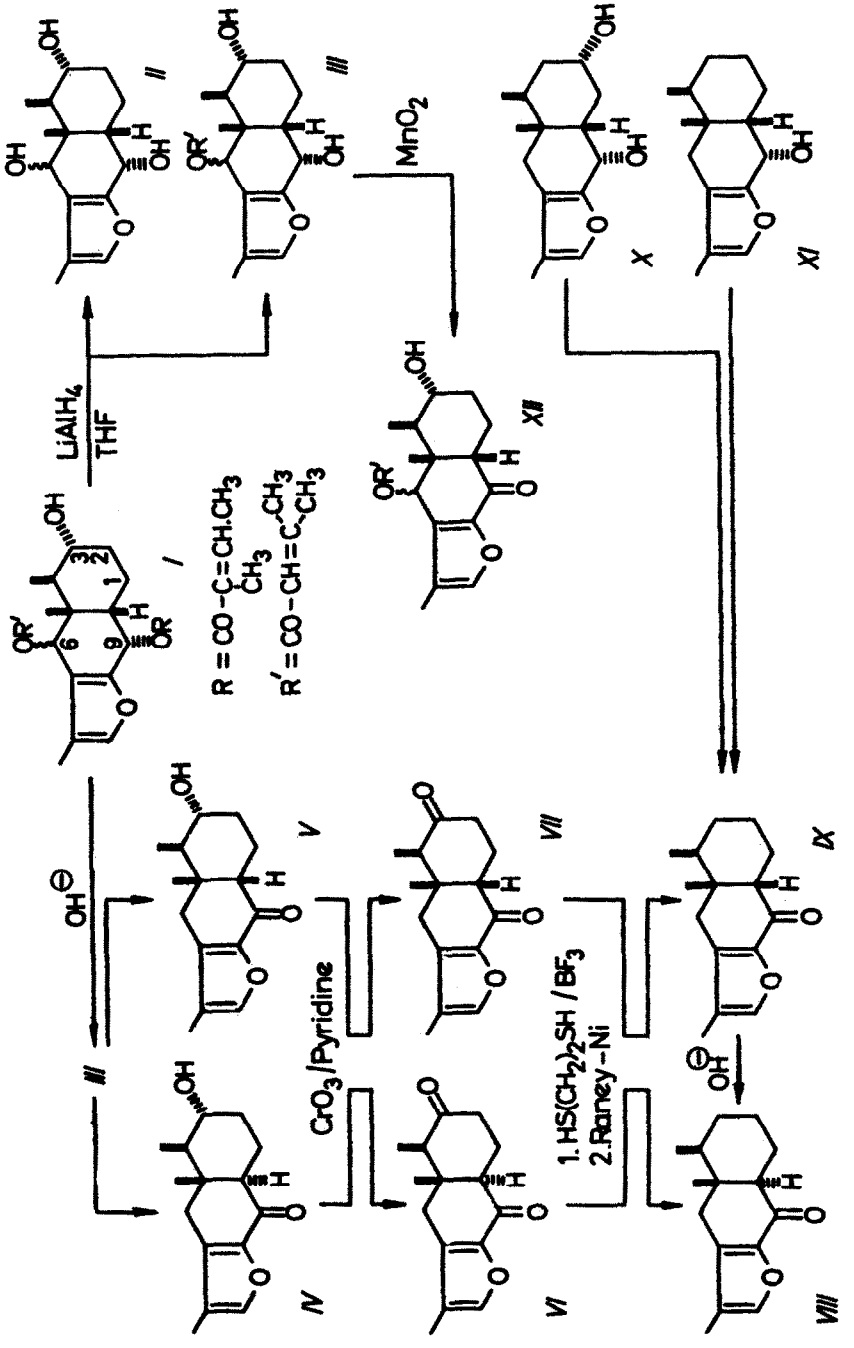
Reduction with lithium aluminum hydride in refluxing tetrahydrofuran gave a mixture of products, from which the triol II, $C_{15}H_{22}O_4$, m.p.202°C, and the monoacyl derivative III, $C_{20}H_{28}O_5$, were isolated.

Brief alkaline hydrolysis of kablicin afforded, in addition to an acidic fraction, also a mixture of neutral compounds which were separated chromatographically on silica. We have isolated the monoester III and two isomeric furoketols $C_{15}H_{20}O_3$: IV, m.p. 230°C, and V, m.p.176°C. These furoketols are cis and trans isomers at C_{10} as inferred from their equilibration with alcoholic NaOH, which gave a mixture of isomers in both cases.

The UV-spectra of both ketols (280 and 282 nm) show that the keto group conjugated with the furan ring is at C_9; this establishes also the position of one of the ester groups of kablicin. Hence, elimination of one hydroxy group, near to the furan ring, took place in the course of the saponification of kablicin. In view of the fact that the triol II does not undergo such an elimination, it is evident that the monoester III must be an intermediate in the elimination. This ester enolizes and saponification leads to the elimination of the hydroxyl, as proved by the isolation of IV and V after alkaline hydrolysis of the monoester III. The course of the reaction establishes unequivocally the position of the additional hydroxyl at C_6.

The acidic fraction after the saponification of kablicin were transformed to the methyl esters and identified by gas-liquid chromatography by comparison with authentic specimens. The mixture contained methyl esters of tyglic acid, angelic acid and β,β-dimethylacrylic acid. The acid fraction after the saponification of the monoester III contained β,β-dimethylacrylic acid alone.

Stereochemical assignments for kablicin was carried out by the degradation of the thioketals of diketones VI, m.p. 225°C, and VII, m.p. 210°C. The diketone VI gave the furoeremophilone VIII, $C_{15}H_{20}O_2$, m.p. 148-149°C, $[\phi](CH_3OH)$ $-8200^\circ_{(295)}$, $0^\circ_{(280)}$, $+9800^\circ_{(255)}$, identical with a compound isolated by us previously from P.hybridus[3]. The diketone VII afforded the furoeremophilone IX, $C_{15}H_{20}O_2$, m.p.112°C, $[\phi](CH_3OH)$ $+8980^\circ_{(297)}$, $0^\circ_{(285)}$, $-14700^\circ_{(260)}$, $0^\circ_{(231)}$, $+3260^\circ_{(225)}$.


LiAlH4
THF
MnO2
R = CO-C(CH3)=CH.CH3
R' = CO-CH=C(CH3)2
OH⊖
CrO3/Pyridine
1.HS(CH2)2SH / BF3
2.Raney-Ni
OH⊖

We prepared furoeremophilone IX by a similar reaction sequence from furanopetasol X, whose absolute configuration is known[5] and also from 9-hydroxyfuranoeremphilone XI, which was recently found to be the principal component of the light petroleum extracts from P.hybridus[6]. Isomerisation with aqueousalcoholic NaOH transforms the cis-annelated furoeremophilone IX to the stable trans-derivative VIII.

The position and the absolute configuration of the free hydroxy group of kablicin at C_3 was established from the PMR spectra of the deuterated diketones VI and VII and the decoupling experiments. The cis-annelation of kablicin was inferred from the ORD curve of XII.

All structural features of the compounds discussed here are in accordance with their PMR-spectra. A detailed discussion of our results with all experimental data will be published in Collection Czech. Chem. Commun.

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