HETEROGENEOUS HYDROGENATION OF 3,7,7-TRIMETHYLCYCLOHEPTA-1,3,5-TRIENE

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It has been shown that the intermediate products of the hydrogenation of 3,7,7-trimethylcyclohepta-1,3,5-triene on platinum black are 2- and 3-carenes, in addition to olefins and dienes of the 1,1,4-trimethylcycloheptane series. The final hydrogenation product contains 96% of 1,1,4-trimethylcycloheptane and 4% of caranes.

The hydrogenation of trienes and, in particular, cyclic trienes is of undoubted interest from the point of view of the investigation of the behavior of conjugated systems in this reaction. The hydrogenation of cycloheptatriene using homogeneous catalysts has been performed [1, 2]. The main products in this case were cyclohepta-1,3-diene and cycloheptene. Only the final reaction products of the heterogeneous hydrogenation of substituted cycloheptatrienes have been described [3]. At the same time, the establishment of the nature of the intermediate products and the study in the change of the composition of the hydrogenate would give information on the occurrence of this reaction in relation to the different degrees of strain of the compounds formed [4].

We have studied the composition of the products of the hydrogenation of 3,7,7-trimethylcyclohepta-1,3,5-triene (I) on platinum black. Compound (I), an unsaturated natural terpenoid [5] is a convenient model for considering hydrogenation reactions. The presence of methyl substituents in it permits a conclusion concerning the direction of the reaction to be drawn in a number of cases without having recourse to such a difficult method as deuteration [1]. The study of the composition of the intermediate products of the hydrogenation of (I) is also important to prove the participation of its tautomer — cara-2,4-diene — in the reaction by analogy with cycloheptatrienes substituted by functional groups [3].

Transformation of (I) in the course of the reaction is illustrated in Scheme 1. The compositions of the hydrogenates are given in Table 1.

Scheme 1
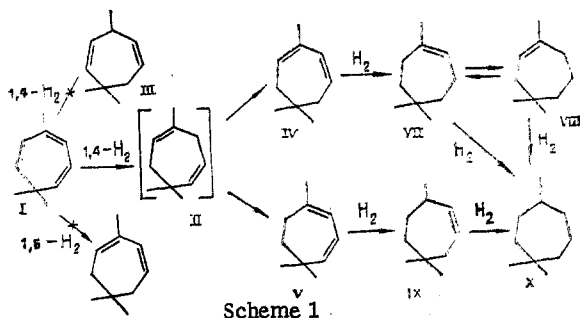
The first stage of hydrogenation is the addition to (I) of 1 mole of hydrogen with the formation of dienes. It has already been reported [1] that 1,6-addition must be excluded from consideration; the absence of such addition was confirmed by experiments with deuteration. 1,4-Addition, the most probable route of the reaction [1] should in the case of (I) give two dienes 2,6,6- and 3,6,6-trimethylcyclohepta-1,4-dienes ((II) and (III), respectively). Neither of these compounds was present in the hydrogenate. This is explained in the first place by the fact that cyclohepta-1,4-dienes are extremely unstable compounds because of the high strain energy of the ring [4]. They readily change into cyclohepta-1,3-dienes by isomerization [6] or a 1,3-hydrogen shift [1]. Furthermore, the existence of (III) is

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TABLE 1. Compositions of Hydrogenates of (I) as a Function of the Amount of Hydrogen Absorbed

| Product	Hydrogen absorbed, moles									
	0,11	0,30	0,62	0,83	1,14	1,32	1,64	2,28	2,57	2,96
	composition of the products, %									
3,7,7-trimethylcyclohepta-1,3,5-triene (I)	94.3	84,6	69,3	59,7	45,5	37,1	24,2	3,3	0.6	—
1,5,5-trimethylcyclohepta-1,3-diene (V)	0,2	0,5	1,1	1.2	1,2	1,8	1,8	0,5	—	—
2,6,6-trimethylcyclohepta-1,3-diene (IV)	0,8	1,9	3,5	4,1	5,0	5,7	5,2	3,1	—	—
3,6,6-trimethylcycloheptane (IX)	1,4	3,8	5,6	7,3	8,5	8,3	6,0	0,9	—	—
1,5,5-trimethylcycloheptane (VIII)	1,4	4,0	8,6	11,2	16,4	18,1	24,6	31,3	27,1	—
1,4,4-trimethylcycloheptane (VII)	0,8	2,1	4,6	6,0	8,9	10,6	13,4	17,0	9,4	—
1,1,4-trimethylcycloheptane (X)	0,5	2,4	5,9	8,7	12,3	15,9	22,0	40,1	59,0	96,0
3-Carene (XII)	0,3	0,3	0,6	0,7	0,9	1,0	1,2	1,6	1,4	Tr.
2-Carene (XIII)	0,1	0,2	0,5	0,6	0,6	0,7	0,7	1,0	0,7	Tr.
Caranes (XIV)	—	0,2	0,3	0,5	0,7	0,8	0,9	1,2	1,8	3,9

apparently impossible because of steric hindrance, as follows from a consideration of molecular models.

2,6,6- and 1,5,5-Trimethylcyclohepta-1,3-dienes ((IV) and (V), respectively) — probable products of the conversions of (II) mentioned above — were found in the hydrogenate. In their turn, as the result of the 1,4-addition of a second mole of hydrogen, (IV) and (V) give 1,5,5-trimethylcycloheptene (VII), which, under hydrogenation conditions, is present in equilibrium with 1,4,4-trimethylcycloheptene (VIII) [7] and 3,6,6-trimethylcycloheptene (IX). Information on the composition of the hydrogenate shows that (V) and the product of its conversion, (IX) are present in the mixture in smaller amounts than (IV) and the corresponding trimethylcycloheptenes (VII) and (VIII). This can be explained on the assumption that the absorption of the diene fragment of (V) on the surface of the catalyst is difficult in comparison with the adsorption of (IV) because of the methyl substituent [8]; in addition, the closeness of the gem-dimethyl grouping probably also opposes adsorption.

On the addition of a third mole of hydrogen, all the trimethylcycloheptenes formed give 1,1,4-trimethylcycloheptane (X), the rate of this reaction being considerably lower than the rate of hydrogenation of the triene and the dienes (see Table).

Since (I) is present in equilibrium with its tautomer cara-2,4-diene (XI), the presence of the stereoisomeric caranes (XIV) in the hydrogenate was to be expected. They are actually formed in the course of the reaction: their final amount was 4%. This ratio ((X):(XIV) = 96:4), of course, does not reflect the proportions of the tautomers in the initial reaction mixture. Although the very fact of the equilibrium is not a matter of any doubt at the present time, in the case of (I) just as in the case of the unsubstituted cycloheptatriene [3], the presence of the bicyclic tautomer has not been detected by any physical methods whatever. The results that we have obtained serve as an experimental confirmation of the existence of this equilibrium for (I).

The comparatively large amounts of caranes in the hydrogenate is probably due to the fact that the planar diene system of (XI) successfully competes with the nonplanar fragment of (I) [9] in the 1,4-addition of hydrogen. In this reaction, compound (XI) must give 3-carene (XII), which isomerizes reversibly into 2-carene (XIII) [7].
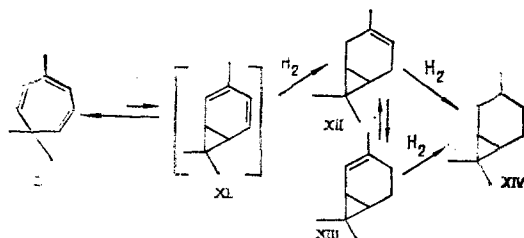
In actual fact, compounds (XII) and (XIII) were present among the reaction products at all stages. Furthermore, as (I) disappeared from the mixture their amount ceased to increase and hydrogenation was completed as soon as all the trimethylcycloheptenes had been hydrogenated.

The hydrogenate was analyzed by the GLC method on a "Vyrukhrom" chromatograph with a FID using packed columns with dimensions of 6000 × 3 mm containing the solid support Chromatone N-AW DMCS with, as the liquid phases (15% of the weight of the support): 1,2,3-tris(β-cyanoethoxy)propane (temperature of analysis 80°C), diethyleneglycol adipate (90°C), and tricresyl phosphate (127°C), and also on a Chrom-4 chromatograph with a FID using a capillary column having dimensions of 50,000 × 0.25 mm containing squalane as the liquid phase at a temperature of analysis of 70°C. The carrier gas was nitrogen.

The individual components were isolated by preparative GLC on a PAKhV-0.5 instrument in a column with dimensions of 8000 × 4 mm containing the solid support Chromatone N-AW DMCS and the liquid phase diethyleneglycol adipate (20%) at a temperature of 95°C with a rate of flow of carrier gas of 60 ml/min.

IR spectra were recorded on a UR-20 spectrophotometer, UV spectra on a Specord-UV spectrometer and PMR spectra on JNCS-100 and Tesla BS-467 (60 MHz) spectrometers with tetramethylsilane as internal standard.

The hydrogenation of 3,7,7-trimethylcyclohepta-1,3,5-triene (I) was carried out in absolute hexane solution on platinum black (5% of the weight of (I)) at a temperature of 20-22°C and pressures of 730-740 mm Hg. To study the change in the composition of the hydrogenate, 1 g of (I) was hydrogenated in 9 ml of hexane; the volume of each of the samples taken was 10 μl (0.01% of the solution).

In order to isolate the intermediate products, 10 g of (I) was hydrogenated under the same conditions until 1.5 moles of hydrogen had been adsorbed.

<u>1,1,4-Trimethylcycloheptane (X)</u> — the final product of hydrogenation — was purified by preparative GLC. Its physical and spectral properties corresponded to those given in the literature [7].

<u>3,6,6-Trimethylcycloheptene (IX)</u> was isolated by preparative GLC in a purity of 98.7%, d_4^{20} 0.8278, n_D^{20} 1.4831. IR spectrum, cm^{-1}: 725, 765, 817, 844, 900, 985, 1022, 1043, 1095, 1133, 1186, 1260, 1325, 1368, 1385, 1448, 1462, 1470, 1630, 1650, 2877, 2905, 2940, 2960, 3020 cm^{-1}. PMR (δ, ppm): 0.92 s (9 H, 3 CH_3) 1.72-1.76 m (4 H, 2 $CH_2<$); 1.80-1.88 m (2 H, CH_2 in the α-position to a double bond); 2.10-2.44 m (1 H, CH); 5.78-5.82 m (2 H, olefinic protons).

<u>1,5,5- and 1,4,4-Trimethylcycloheptenes ((VII) and (VIII))</u> were isolated by preparative GLC, and their physical and spectral properties corresponded to those given in the literature [7].

The presence of 3- and 2-carenes ((IV) and (V)) in the hydrogenate was shown by the method of adding authentic samples, with four liquid phases, which permits the components of a mixture to be identified unambiguously [10].

<u>3-Carene (XII)</u> was isolated from the terpentine of *Pinus sylvestris* L.

<u>2-Carene (XIII)</u> was obtained by the isomerization of 3-carene in the presence of Liethylenediamine [11].

<u>2,6,6-Trimethylcyclohepta-1,3-diene (IV)</u>. The chlorination of 10 g of 1,5,5-trimethylcycloheptene obtained as described by Bardyshev et al. [12] was carried out at −10°C [13]. The mixture of chlorides was boiled in acetic acid with an equivalent amount of NaOAc for 30 min. After cooling and neutralization, hydrocarbons (4.6 g) containing 73% of (IV) were distilled off. The (IV) was isolated by PGLC. IR spectrum, cm^{-1}: 737, 830, 860, 882, 920, 995, 1010, 1127, 1180, 1360, 1375, 1443, 1480, 1612, 1644, 2872, 2910, 2960, 3018 cm^{-1}. PMR (δ, ppm); 0.99 s (6 H, 2 CH_3); 1.81 s (3 H, vinyl CH_3); 2.02-2.11 m (4 H, 2 CH_2); 5.22-5.45 m (3 H, olefinic protons); λ_{max}^{EtOH} 254 nm (log ε 3.72).

<u>1,5,5-Trimethylcyclohepta-1,3-diene (V)</u>. Without preliminary purification, the dehydrochlorination product (see above) was subjected to thermal isomerization at 140°C [14]. Compound (V) was isolated from the isomerizate, which contained 6.6% of (IV) and 58% of (V), by the PGLC method. IR spectrum, cm^{-1}: 737, 828, 861, 886, 970, 1040, 1063, 1127, 1165, 1233, 1270, 1360, 1375, 1450, 1472, 1620, 1654, 2870, 2920, 2960, 3013 cm^{-1}. PMR (δ, ppm): 1.04 s (6 H, 2 CH_3); 1.48-1.59 m (2 H, CH_2); 1.78 s (3 H, vinyl CH_3); 2.08-2.22 m (2 H, CH_2 in the α position to a double bond; 5.28-5.47 m (3 H, olefinic protons). UV spectrum: λ_{max}^{EtOH} 252 nm (log ε 3.88).

SUMMARY

The composition of the products of the hydrogenation of 3,7,7-trimethylcyclohepta-1,3,5-triene on platinum black has been studied.

It has been established that the products of incomplete hydrogenation contains 2- and 3-carenes and caranes, together with compounds having a seven-membered ring. This is confirmation of the tautomeric equilibrium between 3,7,7-trimethylcycloheptatriene and cara-2,4-diene.

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TRITERPENE GLYCOSIDES OF *Climacoptera transoxana*.

II. THE STRUCTURE OF COPTEROSIDE D

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A new tripterpene glycoside, copteroside D, has been isolated from the epigeal part of *Climacoptera transoxana* (Iljin) Botsch. On the basis of chemical transformations and physicochemical characteristics, copteroside D has been ascribed the structure of hederagenin 28-O-β-D-glucopyranoside 3-O-[O-β-D-xylanopyranosyl-(1→ 2)-β-D-glucopyranosiduronic acid].

Continuing a study of the triterpene glycosides of the epigeal part of *Climacoptera transoxana* (Iljin) Botsch. (family Chenopodiaceae), we have isolated from the total extractive substances [1] a compound which we have called copteroside D (II). Quantitatively, it is one of the main glycosides of the plant.

The acid hydrolysis of glycoside (II) yielded the genin (I) which was identified from its physicochemical constants as hederagenin. With the aid of TLC and GLC [2] it was established that the carbohydrate moiety of the copteroside D molecule included residues of D-glucose, D-glucuronic acid, and D-xylose in a ratio of 1:1:1. As has been shown previously [1], copteroside D contains an acylosidic component. To determine the nature of the O-acylosidic moiety, glycoside (II) was subjected to alkaline hydrolysis, as a result of which glycoside (V) was obtained. Acid hydrolysis of the latter showed that it included D-glucuronic