AUTOOXIDATION OF 1,4,4- AND 1,5,5-TRIMETHYLCYCLOHEPTENES

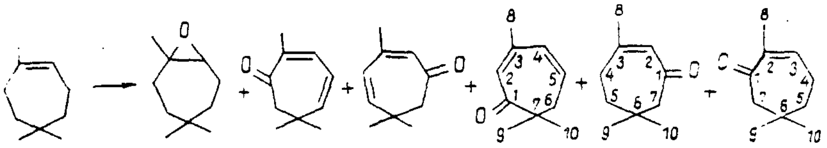
É. N. Manukov and G. N. Bazhina

UDC 547.517

In the oleoresin from Pinus sylvestris we have detected two unsaturated ketones with the 1,1,4-trimethylcycloheptane skeleton: 2,6,6-trimethylcyclohepta-2,4-dienone (I) and 3,6,6-trimethylcyclohepta-2,4-dienone (II). The same ketones had been detected previously in the products of the oxidation of 3-carene [2], one of the main components of domestic turpentines. These facts confirm the genetic linkage of compounds of the 1,1,4-trimethylcyclopentane and carane series.

Of the oxygen-containing compounds present in turpentine, about half have been identified, the isolation of the others being extremely difficult because of their small amount. One of the methods of identification is the use of model compounds in the analysis of mixtures. In order to obtain oxygen-containing compounds with a 7-membered ring we have investigated the products of the autooxidation of 1,4,4- and 1,5,5-trimethylcycloheptenes [(III) and (IV), respectively], synthesized from 3-carene [3]. We have studied the oxidized fraction of the products formed on the prolonged storage of hydrocarbons (III) and (IV) in the air. It has been shown with the aid of GLC that the products included 18-20 components, the amounts of which differed greatly in different samples.

By displacement chromatography on alumina (with pentane—diethyl ether as eluent), from the oxidized fraction of cycloheptene (IV) we have isolated and identified six main components: 1,4,4-trimethyl-8-oxabicyclo[5.1.0]octane (V) (16%), the ketones (I) (18%) and (II) (20%), 3,7,7-trimethylcyclohepta-2,4-dienone (VI) (7%), 3,6,6-trimethylcyclohept-2-enone (VII) (13%), and 2,6,6-trimethylcyclohept-2-enone (VIII) (9%). In the case of the cycloheptane (III), the main component of the oxidized fraction was 1,5,5-trimethyl-8-oxabicyclo-[5.1.0]octane (IX) (54%). In addition to the epoxide (IX) we succeeded in isolating the ketones (I) (10%) and (VII) (16%).



IV V I II VI VII VIII

The individual compounds obtained were identified with the aid of IR and PMR spectroscopies. The properties of the epoxides (V) and (IX) and of the ketones (I) and (II) coincided completely with those given in the literature [4, 1]. The PMR spectra of compounds (VI-VIII) (Bruker WM-360 spectrometer, solvent $CDCl_3$, internal standard TMS) are given in Table 1.

TABLE 1. Chemical Shifts of the Protons, δ, ppm (J, Hz)

Compound	H-2	H-3	H-4	H-5	$6-CH_2$	$7-CH_2$	$8-CH_3$	$9\ CH_3$, $10\ CH_3$
VI	6,40 s	—	5,88 d (6)	6,43 dt (7,2; 6)	2,08 d (7,2)	—	1,80 s	0,96 s 1,23 s
VII	5,87 s	—	2,32—2,36 m	1,56—1,62 m	—	2,42 s	1,93 s	0,99 s
VIII	—	6,61 t (6)	2,27—2,34 m	1,48—1,53 m	—	2,42 s	1,78 s	1,05 s

---

Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 540-541, July-August, 1990. Original article submitted November 15, 1989.

The structures of the components identified show that the process of autooxidation of cycloheptenes takes place in two directions: The first is the addition of oxygen to the double bond with the formation of epoxides, and the second is the allyl oxidation of the methylene groups. In addition to oxidative processes, disproportionation and isomerization of the products formed take place.

LITERATURE CITED

1. O. G. Vyglazov, É. N. Manukov, B. G. Udarov, G. N. Bazhina, T. R. Urbanovich, and L. V. Izotova, Khim. Prir. Soedin., 289 (1989).
2. M. S. Carson, W. Cocker, D. H. Grayson, P. V. R. Shannon, J. Chem. Soc., C., 2220 (1969); I. I. Bardyshev and V. S. Shavyrin, The Autooxidation of Terpene Hydrocarbons; Synthetic Products from Rosin and Turpentine [in Russian], Volgo-Vyatskoe Izd-vo, Gor'kii (1970), p. 211.
3. I. I. Bardyshev, G. V. Deshits, and A. A. Vakhrameeva, Izv. Akad. Nauk BSSR, Ser. Khim., 69 (1980).
4. É. N. Manukov and G. N. Bazhina, Izv. Akad. Nauk BSSR, Ser. Khim. Nauk, 69 (1986).

PECTINS OF TOBACCO STEMS, RICE STRAW, AND KENAF CHAFF

K. K. Kasymalieva, A. A. Khidoyatov, D. A. Rakhimov,
and Z. Dzh. Ashubaeva

UDC 547.458.88

The ever-increasing interest in pectin substances is stimulating the search for new plant sources for industrial production. The pectin substances from sugar beet have been characterized previously [1, 2]. In the present communication we give the characteristics of the pectins from tobacco stems (I), rice straw (II), and kenaf chaff (III).

The plant raw material was first treated with hexane or acetone, eliminating the fatty-waxy fractions [3], and then the pectins were isolated as described in [4].

Information on the amounts of pectin and the results of its analysis are given below:

Raw material; HCl (N of the solution)	Pectin, %	COOH, %	Polygalacturonan, %	Mol., mass
I 0.1	2.6	17.8	79.4	48,000
0.3	3.6	14.3	56.4	27,000
0.4	1.2	8.5	34.3	13,700
II 0.3	2.5	14.0	54.9	25,000
III 0.3	1.2	13.8	54.0	12,300

After the pectin had been obtained, the residue from the raw material was used for the isolation of lignin [5]. The yields were, respectively (%): I – 30; II – 24.2; III – 47.6. On the basis of the results of the complete acid hydrolysis of the pectin its qualitative carbohydrate composition was determined. The percentages of the monosaccharides determined from the results of PC and GLC [6, 7] without taking uronic acid into account are given below:

Pectin	Rha	Ara	Xyl	Man	Glc	Gal
I	5.06	3.16	12.6	--	75.9	3.16
II	6.14	5.58	8.37	11.73	62.56	5.58

Institute of Organic Chemistry, Academy of Sciences of the Kirghiz SSR, Frunze. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 541-542, July-August, 1990. Original article submitted September 28, 1989.