sin) (II), and 5-hydroxy-3-methoxystilbene (monomethyl ester of pinosylvin) (III). The presence of these substances is characteristic for the subgenus Haploxylon of the genus Pinus.

Table 2

Chemical shift, ppm	Nature of the signal	No. of protons	Assignment of the signals
3.75	Singlet	3	Protons of an OCH_3 group
6.25	Doublet, J-3 Hz	1	Protons of a benzene ring A
6.40	" "	1	
6.55	Singlet	1	Proton of a pyrone ring
7.27	" "	—	Solvent $CDCl_3$
7.4—7.8	Multiplet	5	Protons of benzene ring B
12.7	Singlet	1	OH group with an intramolecular hydrogen bond

Substance (I) formed yellow crystals with mp 163–163.5° C (chloroform) and its acetate had mp 151–152° C (80% ethanol).

Substance (II) formed yellow crystals which separated from a mixture of chloroform and ethanol (1:1), mp 275–275.5° C, and its diacetate formed white needles melting at 192–194° C (ethanol). By the cleavage of the chrysin with 30% caustic potash, phloroglucinol and benzoic acid were obtained and were identified by paper chromatography.

Substance (III) separated out from benzene in the form of white plates with a pink tinge having mp 118–119° C, mol. wt. 226 (by mass spectrometry). For all the substances isolated, the results of elementary analysis and the content of functional groups agreed well with the results of theoretical calculations. From the frequencies in the IR spectra of the compounds, the presence of the following fragments in them was established:

Substance	C_6H_5, cm^{-1}	C-O, cm^{-1}	OH, cm^{-1}	C-O-C, cm^{-1}
(I)	1455, 1505, 1620	1658	3610, 3650, 3670	1040, 1270
(II)	1579, 1612	1657	3600, 3640	1169
(III)	1450, 1490, 1590	—	3600, 3650	1060, 1240

Table 1 gives the results of a spectroscopic study of the compounds in the UV region and Table 2 the assignment of the lines of the NMR spectrum for tectochrysin.

The results that we obtained (melting points of tectochrysin and chrysin and their acetates and of the monomethyl ether of pinosylvin) agree with literature data [1].

The samples were given to us by Prof. Erdtman (Sweden) and A. I. Lisina. Students G. Panteleeva and O. Alekseeva took part in the experimental work.

REFERENCE

1. G. Lindstedt, Acta Chem. Scand., 3, 1147, 1949.

9 October 1957

Irkutsk State University

Novosibirsk Institute of Organic Chemistry, Siberian Division, AS USSR

UDC 547.913+542.91

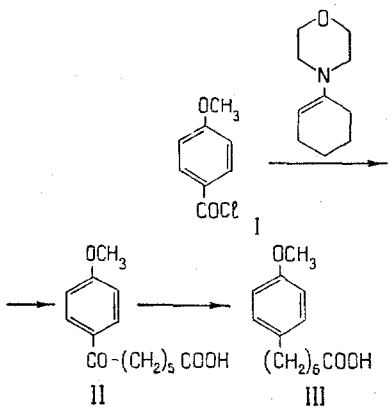
STUDIES OF SUBSTANCES FOUND IN ESSENTIAL OILS. XXXV

M. I. Goryaev, F. S. Sharipova, L. K. Tikhonova, and L. A. El'chibekova

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 4, pp. 250–251, 1968

Continuing work on the synthesis of physiologically active substances from terpenoids [1, 2] we have carried out the synthesis of ω-(p-methoxyphenyl)heptanoic acid.

To build up the side chain we used the method of condensing an enamine with anisoyl chloride (I), which has been employed widely in recent years in the synthesis of acids [3]. In our case as the enamine we chose 1-morpholinocyclohexene, prepared from morpholine and cyclohexanone in the presence of p-toluenesulfonic acid by a known method [4].



The keto acid (II) with mp 132–133° C, and the composition $C_{14}H_{18}O_4$ was obtained. The IR spectrum of the acid contained, in addition to frequencies characteristic for a carboxy group (1718 cm^{-1}) a frequency of 1680 cm^{-1} due to a carbonyl group conjugated with an aromatic nucleus. In addition, the frequencies 2872 and 2935 cm^{-1} show the presence of methylene groups in the molecule of the substance and the frequencies 1412 and 1430 cm^{-1} relate to methylene groups in the α-position with respect to the carbonyl. The keto acid (II) forms a 2, 4-dinitrophenylhydrazone with mp 115–117° C, $C_{20}H_{22}O_7N_4$.

The keto acid was reduced by a modification of the Kizhner-Wolff [Wolff-Kishner] method [5] to the acid (III). In the spectrum of this acid, the frequency of the carbonyl group had disappeared and the intensity of the frequency due to the methylene groups (2935 cm^{-1}) had increased, and a methylene group had also remained in the α-position to a carbonyl group (1412 cm^{-1}).

REFERENCES

1. M. I. Goryaev, L. A. Ignatova, G. A. Tolstikov, and A. D. Dembitskii, ZhOKh, 35, 1186, 1965.
2. M. I. Goryaev, F. S. Sharipova, L. K. Tikhonova, and L. A. El'chibekova, KhPS [Chemistry of Natural Compounds], 3, 131, 1967.
3. Keiiti Sisido and Mitudosi Kawanisi, J. Org. Chem., 27, 3722, 1962.
4. Collection: Synthesis of Organic Preparations, Moscow [in Russian], no. 12, 1964.
5. Huang Minlon, J. Amer. Chem. Soc., 68, 2487, 1946.

7 July 1957

Institute of Chemical Sciences AS KazSSR

UDC 547.913.001.2

A NEW TERPENE HYDROCARBON — ACHILLENE

A. D. Dembitskii, R. A. Yurina, and M. I. Goryaev

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 4, p. 251, 1968

In a study of the essential oil of Achillea filipendulina (fernleaf yarrow), from the fraction boiling at 60–65° C (40 mm Hg) by preparative gas-liquid chromatography, we isolated a substance possessing a strong peculiar odor and characterized by the following constants: n_D^{20} 1.4526, d_{20}^{20} 0.7836, $[\alpha]_D^{20}$ +64°, MR_D 46.87. The molecular weight of the substance isolated, determined by mass spectrometry, was 136.

Strong bands at 890, 914, 998, 1636, and 3079 cm^{-1} in the IR spectrum of the substance show the presence in its molecule of one vinyl $-CH=CH_2$ group and one methylene $C=CH_2$ group. The low intensity of the 1667 cm^{-1} band and the moderate intensity of the 667 cm^{-1} band are apparently due to the presence of a third multiple $-CH=CH-$ bond. This is shown by the presence of a strong band at 1659 cm^{-1} in the Raman spectrum of the substance.

The infrared and electronic spectra of the hydrocarbon confirm the absence of conjugation between its multiple bonds.