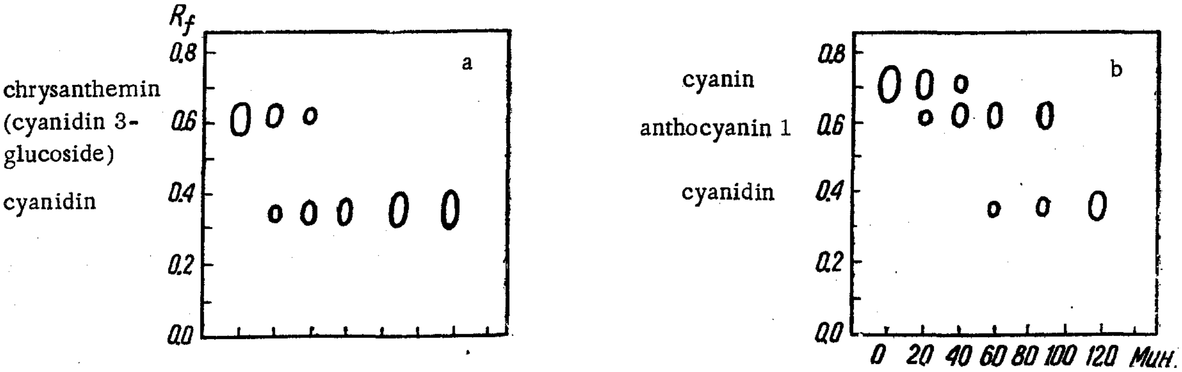
	λ, mμ	D	E_{440}/E_{max}, %
Anthocyanin 1 ($6 \cdot 10^{-6}$ mole/l)	526	0.290	22
	440	0.065	
Anthocyanin 2 ($4.6 \cdot 10^{-6}$ mole/l)	524	0.257	12
	440	0.031	

By paper chromatography in the systems butan-1-ol–hydrochloric acid–water (7:2:5); acetic acid–hydrochloric acid–water (3:1:8), (5:1:5), (30:3:10), and (15:3:82); butan-1-ol–acetic acid–water (4:1:5); and m-cresol–acetic acid–water (50:2:48), anthocyanin 1 was identified as cyanidin 3-monoglucoside (chrysanthemin) and anthocyanin 2 as cyanidin 3, 5-diglucoside (cyanin).



One-dimensional ascending chromatograms of the products of the stepwise hydrolysis of anthocyanin 1 (a) and of anthocyanin 2 (b) in the glacial acetic acid–concentrated hydrochloric acid–water (5:1:5) system.

The stepwise hydrolysis [2] (figure) of anthocyanin 1 confirmed its identification as cyanidin 3-monoglucoside (chrysanthemin) and that of anthocyanin 2 as cyanidin 3, 5-diglucoside (cyanin), since the stepwise hydrolysis of the latter at the stage of the formation of a monoglucoside a yellow spot with R_f 0.74 appeared as well as the spot of cyanidin 3-monoglucoside. According to Willstätter [3], 5-monosides possess a yellow fluorescence.

REFERENCES

1. J. B. Harborne, Biochem. J., 70, 22, 1956.
2. J. Abe and K. Hayashi, Bot. Mag. Tokyo, 69, 577, 1956.
3. R. Willstätter and J. Burdick, Liebigs Ann. Chemie., 412, 149–164, 1916.

4 January 1966

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PRODUCTION OF AMINES OF LINOLOOL

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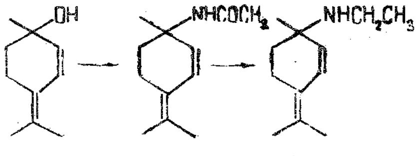
Khimiya Prirodnykh Soedinenii, Vol. 3, No. 1, p. 60, 1967

In order to obtain substances with gangliolytic activity, we have carried out the synthesis of an amine from linolool. It is known that only secondary amines possess appreciable activity [1, 2], while it is essential for high activity that one of the radicals connected to the nitrogen is a methyl or an ethyl group. Consequently, as the nitrile component of Ritter's amide condensation reaction [3] we used acetonitrile and made a detailed study of the behavior of linolool under the conditions of this reaction. It was found that the condensation of one mole linolool [1] in the presence of two moles of acetonitrile takes place with the highest yield at –5° to 10° C. Under these conditions, the yield of 6-acetylamino-2, 6-dimethylocta-2, 7-diene (II) (mp 120–121° C) was 45%.

Reduction of the acetamide (II) with lithium aluminum hydride in absolute ether gave 6-ethylamino-2, 6-dimethylocta-2, 7-diene (III) and the corresponding hydrochloride with mp 167–170° C.



I II III

REFERENCES

1. N. K. Kochetkov et al., ZhOKh, 29, 3613, 1959.
2. N. K. Kochetkov et al., ZhOKh, 31, 3601, 1961.
3. J. J. Ritter et al., J. Amer. Chem. Soc., 73, 4076, 1956.

10 August 1966 Institute of Chemical Sciences, AS KazSSR, Alma-Ata

THE NATURE OF THE DITERPENE DIOL FROM THE OLEORESIN OF LARIX SIBIRICA

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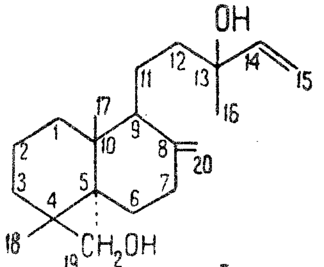
Khimiya Prirodnykh Soedinenii, Vol. 3, No. 1, pp. 61–62, 1967

We have previously [1] isolated a diterpene diol $C_{20}H_{34}O_2$ with mp 108.5° C from the neutral fraction of the oleoresin of Larix sibirica Lebd. (Siberian larch). From the results of hydrogenation and dehydrogenation and from the identity of the IR spectrum of the monoacetate of the diol with the IR spectrum of larix acetate [2], we assumed that the diol isolated was larixol [2–6], although its melting point was somewhat higher than that of larixol (101° C).

A further study of the diol has shown that its NMR specturm (taken on an instrument with an operating frequency of 60 MHz and with tetramethylsilane as internal standard) has three signals of equal intensity in a strong field at 9.30 τ, 8.82 τ, and 8.58τ, which are due to methyl groups at C_{17}, C_{18}, and C_{13}, respectively. From its chemical shift, a multiplet with its center at 6.30 τ corresponds to a methylene group connected to an atom of oxygen (CH_2O). This multiplet, consisting of four lines at 6.59 τ, 6.41 τ, 6.19 τ, and 5.99 τ, is characteristic for two nuclei of the AB type (C_{19}). In a weak field, it is possible to isolate, in the 5.20–3.78 τ region, the signal of an exocyclic methylene group (C_{20}) and also a group of signals belonging to a AB_2 system of nuclei (C_{14}–C_{15}).

These results suggest structure (I) for the diol:



I

Oxidation of the diol with chromic anhydride in pyridine gave an aldehyde with n_D^{20} 1.5210, the semicarbazone of which had mp 193–195° C.

The IR spectrum of the aldehyde shows characteristic absorption bands at 1710, and 2720 (CO) cm^{-1}. From its refractive index and IR spectrum, the aldehyde is similar to torulosal [7] but it did not give the crystalline complex with carbon tetrachloride that is characteristic for the latter.

Reduction of the aldehyde with hydrazine hydrate led to a monohydric alcohol $C_{20}H_{34}O$ with mp 38.5–39.5° C, $[\alpha]_D^{20}$ + 50° (c 2.65; chloroform), the IR spectrum of which and a mixed melting point showed that it was identical with epimanool [4]. On direct comparison, the initial diol proved to be 13-epitorulosol [8, 9], and not larixol.