Isolation of Ulugbin (IX). On standing, fraction B deposited a precipitate which, after recrystallization from hexane–methanol, consisted of colorless scale-like crystals with mp 215°C, R_f 0.17.

SUMMARY

From the herbage of Ulugbekia tschimganica (B. Fedtsch.) Zak two new phenolcarboxylic acids have been isolated in the form of their methyl derivatives: methyl ulugbekate $C_{19}H_{18}O_6$ (I) and methyl ulugbinate acid $C_{20}H_{22}O_7$ (II), mp 228°C.

It has been established that (I) most probably has the structure of 1,5-bis(3',4'-dihydroxyphenyl)-3-methoxycarbonylpent-1-ene and (II) that of 1,5-bis(2',4'-dihydroxyphenyl)-3-methoxycarbonylpent-1-ene and (II) that of 1,5-bis(2',4'-dihydroxyphenyl)-3-methoxycarbonyl-4-methoxypent-2-ene.

The presence of fumaric, caffeic, and chlorogenic acids, and also of mono and dimethyl fumarates has been established chromatographically.

The roots have yielded a new phenolic terpenoid, $C_{16}H_{20}O_4$, for which 3-(2,4-dihydroxyphenyl)-1-(5,5-dimethyltetrahydropyran-2-ylidene)propene has been suggested as one of the most likely structures.

LITERATURE CITED

1. H. Wagner, L. Hörhammer, and U. Frank, Arzneim.-Forsch., 20, No. 5, 705 (1970).
2. F. X. Gasner, M. L. Hopwood, W. Johnson, and S. G. Sunderwirth, Proc. Soc. Exp. Biol. Med., 114, No. 1, 20 (1963).
3. V. M. Dil'man, I. S. Kozhina, L. A. Klyuchnikova, M. N. Kibal'chich, and Yu. Yu. Kusov, Vopr. Onkol., 14, No. 7 (1968).
4. G. Johson, S. G. Sunderwirth, H. Gibian, A. W. Coulter, and F. X. Gasner, Phytochemistry, 2, 145 (1963).

SOME PRODUCTS OF THE COUPLING OF GOSSYPOL WITH DIAZOTIZED AMINES

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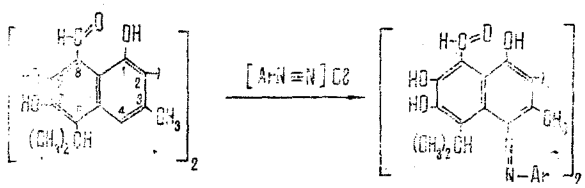
In order to find methods for the practical utilization of gossypol, we have obtained some products of the coupling of gossypol with diazotized amines which are capable of dyeing cotton fabrics.

Usually, in the reaction of diazonium salts with aromatic amines or phenols the azo group enters the para or ortho position to the amino or hydroxy group [1]. Markman and Zalesov have succeeded in introducing a diazo group into the gossypol molecule by coupling with diazonium salts [2].

Since the gossypol molecule contains two unsubstituted hydrogen atoms (4,4') present in the para position to the 1,1'-hydroxyls, the coupling reaction of gossypol with aromatic diazo compounds should take place with the formation of a symmetrical compound:



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As the initial amines for obtaining the diazonium compounds we used p-nitroaniline, α-naphthylamine, benzidine, aniline, and sulfanilic acid. The coupling of gossypol with these diazonium compounds gave a series of its azo derivatives. The elementary analyses of these products showed that the reaction between an aromatic diazonium compound and gossypol leads to the introduction of only one azo group $-N = N-Ar-$ into the symmetrical gossypol molecule.

The color of all these substances is due to the presence of the chromophoric groups $> C = C <$, $>C = O$, and the azo group $-N = N-$ in their molecules, and the presence of an auxochromic group – a hydroxyl in the para position to the diazo group – is responsible for the dyeing properties of its azo derivatives.

The products obtained were tested as dyes for cotton fabric. Phenylazogossypol dyed the fabric yellowish-orange; p-nitrophenyl- and α-naphthylazogossypols, orange-red; and diphenyldi(azogossypol), red.

p-Nitrophenylazogossypol, $C_{36}H_{33}O_{10}N_3$, is the product of the coupling of gossypol with diazotized p-nitroaniline with the introduction of one $-N = N-C_6H_4NO_2$ group into its molecule in the 4 or 4' position. This substance is a bright orange crystalline powder with mp 215°C.

α-Naphthylazogossypol, $C_{40}H_{36}O_8N_2$, is formed on coupling gossypol with diazotized α-naphthylamine. It is a uniform claret-beetroot-colored powder with mp 180°C.

Diphenyldi(azogossypol), $C_{72}H_{66}N_4O_{16}$, which is formed by the coupling of two molecules of gossypol with one molecule of diazotized benzidine, is a uniform dark red powder with mp 145°C.

Phenylazogossypol, $C_{36}H_{34}O_8N_2$ – the product of the coupling of gossypol with diazotized aniline (introduction of the $-N = N-C_6H_5$) group into the gossypol molecule – is an orange crystalline powder with mp 150°C.

None of the azo derivatives of gossypol mentioned is soluble in water and they are all readily soluble in ethanol, acetone, and diethyl ether. The presence of a sulfo group in the molecule of the azo compound imparts an acid nature to it and makes it soluble in water, as can be seen for the case of the coupling of gossypol with diazotized sulfanilic acid.

p-Sulfophenylazogossypol, $C_{36}H_{34}O_{11}SN_2$, is a pale orange crystalline powder.

EXPERIMENTAL

Diazotization. The reaction was performed at low temperature with constant stirring. During the reaction, the presence of mineral acids was checked by means of Congo Red paper and that of nitrous acid by means of starchiodide paper. Several methods of diazotization were used according to the nature of the amine involved [3].

Sulfanilic acid is sparingly soluble in water, and therefore it was converted into the sodium salt [4]. For coupling we used gossypol that we obtained by the diethyl ether extraction of previously defatted and moistened cottonseed meal [5]. After repeated recrystallization from petroleum ether, the gossypol had mp 176°C.

Immediately before the coupling of the gossypol with the diazonium salts obtained by diazotization, the excess of hydrochloric acid was removed from them by treatment with sodium acetate, the reaction being checked by means of Congo Red. Then the solution of the diazonium compound was added to an ethanolic solution of the gossypol (0.1 g in 50 ml of ethanol). A precipitate was formed which was readily soluble in an excess of ethanol. The reaction was performed at 0-5°C with constant stirring. To check the course of the reaction and to determine the moment of its completion we used a solution of β-naphthol [3]. The reaction was considered complete when an excess of diazonium compound was found in the reaction mixture.

The dyeing of samples of cotton fabric by the substances obtained was performed by the ice-dyeing method [6]. The dyed fabric was left in the air for complete coagulation and drying and was then heated in a solution of sodium carbonate and soap to improve the shade of the dyeing.

The fabric acquired a uniform fast color.

SUMMARY

A series of products of the coupling of gossypol with diazotized amines has been obtained. It has been established that they are monoadducts. The possibility of using them as dyes for cotton fabric has been shown.

LITERATURE CITED

1. P. Karrer, Organic Chemistry, Fourth English ed., Elsevier, Amsterdam (1950).
2. A. L. Markman and Yu. P. Zalesov, Maslob.-Zhir. Prom., No. 3, 8 (1960).

3. Preparative Organic Chemistry [in Russian], Moscow (1959), p. 55.
4. Modern Experimental Methods in Organic Chemistry [in Russian], Moscow (1960), p. 224.
5. A. L. Markman and V. P. Rzhekhin, Gossypol and Its Derivatives [in Russian], Moscow (1965), p. 18.
6. N. I. Amiantov, The Chemistry and Technology of Intermediates and Dyes [in Russian], Moscow (1949), p. 149.

SCHEME FOR THE GROUP SEPARATION OF THE COMPONENTS OF CONIFER OLEORESINS. TERPENOIDS OF THE OLEORESIN OF Pinus cembra

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The oleoresins of conifers consist of very complex mixtures of terpenoids sometimes also containing paraffinic hydrocarbons [1]. Their analysis usually includes preliminary separation into acidic and neutral fractions. The acidic fraction is methylated with diazomethane and investigated by GLC, and the neutral fraction is separated by chromatography into a hydrocarbon fraction and a fraction of oxygen-containing compounds or is subjected directly to vacuum distillation. In both cases, the neutral substances are then subjected to repeated chromatographic separation in order to isolate individual components. The closeness of their adsorption properties and the lability of the terpene compounds considerably complicate the process of chromatographic separation and make it difficult to evaluate quantitatively the amounts of the characteristic types of terpenoids and of individual compounds. The latter aspect of the problem is particularly pronounced with the use of high-temperature vacuum distillation for the preliminary separation of the neutral fraction.

The presence in all conifer oleoresins of certain classes of neutral and acidic terpene components (hydrocarbons, aldehydes, resin acids, etc.) makes it possible to separate the oleoresin into groups of compounds by using the differences in the adsorption and chemical properties of these groups. Such a separation can be performed by a scheme which we have tried out on the oleoresins of the Korean pine [2] and the Japanese atone pine [3]. It will probably be suitable for the separation of the oleoresins of other types of conifers, as well.

A reduction in the probability of the formation of by-products from the native compounds is achieved by using air-dry SiO_2 for chromatography at all stages of this scheme. To separate the hydrocarbons from the fraction of neutral oxygen-containing compounds it is possible to use Al_2O_3 (activity grade III). In all cases, the eluent is petroleum ether (bp 40-70°C) with increasing concentrations (from 0 to 100%) of diethyl ether. Analytical TLC on SiO_2, which is used to check the separation of the fractions of neutral oxygen-containing compounds and of the methylated acid fraction of the oleoresin, is performed with the same solvents. This separation is performed with the aid of marker substances. All the substances having R_f values greater than the marker substance isocembrol (or manool, epimanool, or cis-abienol, which have the same R_f value on SiO_2) pass into the fraction of oxides, esters, and carbonyl compounds. All substances having the same R_f as isocembrol pass into the second fraction (nonpolar monohydric alcohols. The fraction of polar monohydric alcohols includes substances having R_f values lower than that of isocembrol and greater than that of the second marker substance, pinusolide. The separation of the monohydric alcohols into two fractions is due to the fact that the less polar tertiary diterpene alcohols are frequently comparatively well separated from the more polar primary diterpene alcohols. These two groups of alcohols are common components of conifer oleoresins and their separation is therefore justified. All substances having R_f values equal to or smaller than that of pinusolide pass into the fraction of di- and polyfunctional compounds. (See scheme on following page).

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