gram and was refined in the usual way [11] to R = 0.087 and R_w = 0.065. The coordinates of the nonhydrogen atoms are given in Table 1.

SUMMARY

The photochemical intramolecular cyclization of an α-enol of the cembrene series, leading to a higher isoprenolog of the bourbonane sesquiterpenes has been performed for the first time.

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DITERPENOIDS OF *Pulicaria salviifolia*.

II. STRUCTURE OF SALVICIN

M. R. Nurmukhamedova, N. D. Abdullaev,
and G. P. Sidyakin*

UDC 547.595.9

A new diterpenoid acid of the clerodane series, $C_{20}H_{32}O_4$, $[\alpha]_D^{20}$ −75.4° (c 0.26; methanol), which has been called salvicin, and the known flavonoid rutin have been isolated from a chloroform extract of the epigeal part of *Pulicaria salviifolia*. The structure of salvicin has been established on the basis of spectral characteristics and chemical transformations.

Continuing a study of the components of *Pulicaria salviifolia* Bunge (family Asteraceae) [1], we have isolated a new diterpenoid acid of the clerodane series which we have called salvicin (I). No diterpenoid acids of this series have previously been found in plants of the USSR flora.

Salvicin (I) has the elementary composition $C_{20}H_{32}O_4$ (M^+ 336) and is readily soluble in aqueous solutions of sodium bicarbonate. The acid nature of salvicin is shown by the presence in its IR spectrum of a broad band corresponding to the hydroxyl of a carboxy group at 2380-2680 and a strong absorption band at 1680 cm^{-1} which is assigned to an acid carbonyl, and also by the presence in the mass spectrum of a peak with m/z 291 which characterizes the splitting out of a carboxy group from the molecular ion (M^+ − COOH) [2]. In addition, in the PMR spectrum of (I) (C_5D_5N, 0 is TMS), a broadened one-proton singlet is observed at 8.76 ppm corresponding to the proton of a carboxy group. In analogy with compounds isolated previously [1], the PMR spectrum of salvicin has the signals of the protons of three methyl groups — two singlets at 1.57 and 0.74 ppm and a doublet at 0.79 ppm with ^3J = 6.7 Hz — and the broadened

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*Deceased.

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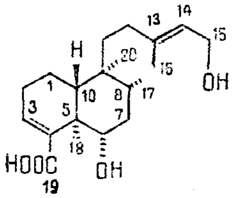
triplet of an olefinic H-3 proton at 7.07 ppm with $\Sigma^3J = 7.9$ Hz. These facts in combination with the elementary composition of the substrate permit salvicin to be assigned to the bicyclic diterpenoids of the clerodane series [3-5]. The proton at C-6 is geminal to a hydroxy group and, similarly to the lactone proton of salvin, isolated previously from the same plant [1], gives a quartet at 4.01 ppm with ^3J = 10.6 and 5.1 Hz, i.e., showing by its position and the nature of its splitting the β-axial orientation of H-6.

An analysis of the IR and mass spectra of (I) showed the absence of a furan ring from the salvicin molecule [5-7]. The absence of a furan ring from salvicin and the appearance in the PMR spectrum of (I) of the signal of another olefinic proton at 5.81 ppm (t, Σ^3J = 13 Hz), of a two-proton doublet at 4.53 ppm (^3J = 6.7 Hz) from a methylene group attached to a heteroatom, and of the signal of the protons of a methyl group on a double bond at 1.73 ppm permitted the conclusion that the side chain of the (I) molecule contained in place of a furan ring the fragment $-(CH_3)C{=}CH{-}CH_2OH$.



This is the first time that such a type of aliphatic side chain has been found for clerodane diterpenoids. On the basis of what has been said above, for salvicin we suggest the structure of 19-carboxy-6α,15-dihydroxy-trans-cleroda-3,13(14)-diene.

Together with salvicin, in the polar fraction from *Pulicaria salviifolia* we detected the flavonoid rutin, which was identified by a mixed melting point with an authentic sample.

EXPERIMENTAL

General Observations. The conditions of recording the spectra have been described in [1].

Isolation of Salvicin. The dried and comminuted epigeal part (9 kg) of the plant *Pulicaria salviifolia* collected in September, 1981 (village of Khonabad, Pap region, Namangan province) was exhaustively extracted with chloroform (4×). The concentrated chloroform extract was dissolved in 2.5 liters of ethanol, and 1.6 liters of hot water was added. The precipitate that deposited was filtered off. The ethanolic solution of the extractive substances was washed successively with hexane and benzene. The residual aqueous ethanolic solution was concentrated. The weight of the residue was 80 g. The sum of the extractive substances was deposited on a column of silica gel and was eluted with the hexane–chloroform (1:2) and chloroform systems. When the column was eluted with the hexane–chloroform (1:2) system, 8 g (0.09% of the weight of the dry raw material) of rutin was isolated, and elution with chloroform gave 7 g of salvicin (0.08%).

Salvicin (I) formed a crystalline substance with a creamy tinge, $C_{20}H_{32}O_4$, M^+ 336, mp 157-158°C, $[\alpha]_D^{20}$ −75.4° (c 0.26; methanol). R_f 0.13 (hexane–ethyl acetate (1:1)). IR spectrum, ν_{max}^{KBr} (cm^{-1}): 2380-2680, 1680. Mass spectrum, m/z (%); 336 (M^+) (18); 321 $(M - CH_3)^+$ (20); 318 $(M - H_2O)^+$ (80); 219 (100). CD: $[Q]_{248}$ = +5404,96, ΔE = +1.63, $[Q]_{211}$ = −18697.6, ΔE = −5.6. Rutin, $C_{27}H_{30}O_{16}$, mp 186-190°C, was identified by a mixed melting point with an authentic sample.

SUMMARY

From the epigeal part of *Pulicaria salviifolia* Bunge (family Asteraceae) have been isolated the main flavonoid rutin and a new diterpenoid acid of the clerodane series — salvicin — the structure of which has been established.

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GLYCOSYLATION OF TRITERPENOIDS OF THE DAMMARANE SERIES.

IV. β-D-GLUCOPYRANOSIDES OF BETULAFOLIENETRIOL AND ITS DERIVATIVES

L. N. Atopkina, V. A. Denisenko
V. L. Novikov, and N. I. Uvarova

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The glycosylation of betulafolienetriol (dammar-24-ene-3α,12β,20(S)-triol) under the conditions of the Koenigs–Knorr, the Helferich, and the orthoester methods has been studied. It has been shown that the condensation of β-folienetriol and its 3-epimer with α-acetobromoglucose in the presence of silver oxide leads to a mixture of the corresponding 3-, 12-, and 20-mono- and 3,12- and 3,20-di-O-β-pD-glucopyranosides. It has been established that the glycosylation of dammar-24-ene-3α,12β,20(S)-triol under Helferich's conditions and those of the orthoester method is accompanied by a side reaction of dehydration in the side chain and leads to 20-dehydroxy derivatives. The structures of all the newly obtained compounds have been established on the basis of the results of IR and of ^{1}H and ^{13}C NMR spectroscopy.

Pharmacological and biochemical investigations performed in recent years have shown that the stimulating and adaptogenic action of extracts of the roots of *Panax ginseng* is due to the saponins present in it [1-3].

The bulk of the saponins from the roots of *Panax ginseng* is divided into two groups: the ginsenosides R_d, R_c, R_{b1} and R_{b2}, the aglycon of which is 20(S)-protopanaxidiol [dammar-24-ene-3α,12β,20(S)-triol] (I) and the ginsenosides R_{g1}, R_{g2}, R_e, and R_f, the aglycon of which is 20(S)-protopanaxatriol [dammar-24-ene-3α,6α,12β,20(S)-tetraol] [4, 5]. As a rule, the carbohydrate chains are located at the third, sixth, or twelfth hydroxyls.

A triterpene of the dammarane series, betulafolienetriol (II), which was first isolated by Fischer and Seiler [6] from the European white birch *Betula alba* and was later found in the leaves of Far Eastern species of the genus *Betula* [7], differs from the native genin of the ginsenosides R_{b1}, R_{b2}, R_c, and R_d only by the configuration of the hydroxy group at C-3. The unique physiological action of ginseng and its poor distribution in nature makes it desirable to find possible methods of synthesizing glycosides close in structure to the ginsenosides from the comparatively readily available betulafolienetriol (II) and from its 3-epimer (I), which can easily be obtained from (II) by oxidation to the 3-keto derivative (III) followed by reduction.

The extremely limited information available in the literature [8] on the production of glycosides from the triterpenoids isolated from the birch contains no details of the methods of glycosylation used or proofs of the structure and individuality of specific glycosides.

Continuing a study of the glycosylation of dammarane triterpenoids, we have performed the condensation of triols (I) and (II) and their 3-O-acetates (IV) and (V) with α-acetobromoglucose under the conditions of the Koenigs–Knorr reaction. The results of the experiments are given in Table 1.

The glycosylation of the triols (I) and (II) with α-acetobromoglucose in methylene chloride in the presence of silver oxide at room temperature (Table 1, expts. 1 and 2) led to mul-

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Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Science Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 301-312, May-June, 1986. Original article submitted November 18, 1985.