FLAVONOIDS OF Ammothamnus lehmannii.

STRUCTURE OF LEHMANNIN AND OF AMMOTHAMNIDIN

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The new flavanon lehmannin (I) has been isolated from the roots of Ammothamnus lehmannii Bunge. On the basis of chemical transformations and with the aid of physicochemical characteristics it has been established that compound (I) has the structure of 2',4',7-trihydroxy-8-(2"-isopropenyl-5"-methylhex-4"-enyl)flavanone. The alkaline cleavage of lehmannin gave ammothamnidin (V). The structure proposed previously for the chalcone ammothamnidin has been corrected. It has been shown that it has the structure of 2,2',4,4'-tetrahydroxy-3'-(2"-isopropenyl-5"-methylhex-4"-enyl)chalcone. A comparative study of the ^{13}C NMR spectra of a number of flavanones has revealed an empirical law permitting the prediction of the presence or absence of substituents (OH and OCH_3) at C-2' from the value of the chemical shift of the signal of the C-2 carbon atom.

The sum of the pigments has been isolated from the roots of the plant Ammothamnus lehmannii Bunge and has been called soforeol [1, 2]. However, the chemical nature of the pigments of this plant has remained unelucidated until recently. In the preceding paper we reported the isolation and study of the chemical structure of a new chalcone ammothamnidin [3]. Continuing this investigation, from the roots of the plant collected in the environs of Lake Shurkul', Dzhambul province, KazSSR, in addition to ammothamnidin a new flavanone, which has been called lehmannin (I), has been isolated. The present paper is devoted to a proof of the structure of lehmannin. In addition, the previously proposed structure of ammothamnidin has been corrected.

Lehmannin has the empirical formula $C_{25}H_{28}O_5$, and on reduction with magnesium in hydrochloric acid forms a yellow coloration. The IR spectrum of (I) contains absorption bands of hydroxy groups (3270-3100 cm^{-1}), of the carbonyl of a γ-pyrone ring (1648 cm^{-1}), of aromatic C=C bonds (1605, 1590, 1540 cm^{-1}), and of a terminal methylene group (875 cm^{-1}). The PMR spectrum of lehmannin exhibits the signals of the H-2 (6.13 ppm, 1 H, dd, J = 11.0 and 5.0 Hz) and H-3 (2.88-3.28 ppm, m) protons that are characteristic for the heterocyclic ring of flavanones [4].

The fact that lehmannin belongs to the flavanone group was also shown by absorption maxima in the UV spectrum at 242* (inflection), 288, and 313* nm [4, 5] and by the signals of the C-2 and C-3 carbon atoms at 75.0 ppm and 43.2 ppm, respectively, in the ^{13}C NMR spectrum [6, 7]. The acetylation of lehmannin gave the triacetyl derivative (II) the PMR spectrum of which contained the signals of the protons of the methyl radicals of three aromatic acetoxy groups at 2.18, 2.21, and 2.23 ppm (3 H, s, each). The methylation of (I) with an ethereal solution of diazomethane led to the trimethyl ether (III) with the composition $C_{28}H_{34}O_5$, M^+ 466, containing no free phenolic hydroxy groups.

Thus, of the five oxygen atoms of the molecule of (I) three belong to phenolic hydroxy groups and two are present in a γ-pyrone ring. The presence in the ^{13}C NMR spectrum of lehmannin of the signals of four aromatic carbon atoms (155.7, 158.6, 162.5, and 136.0 ppm) linked with oxygen, and of the carbon of a carbonyl group (192.6 ppm) is in harmony with the facts given above.

The absence of a bathochromic shift in the UV spectrum on the addition of aluminum trichloride and the value of the chemical shift of the signal of the carbon atom of the carbonyl

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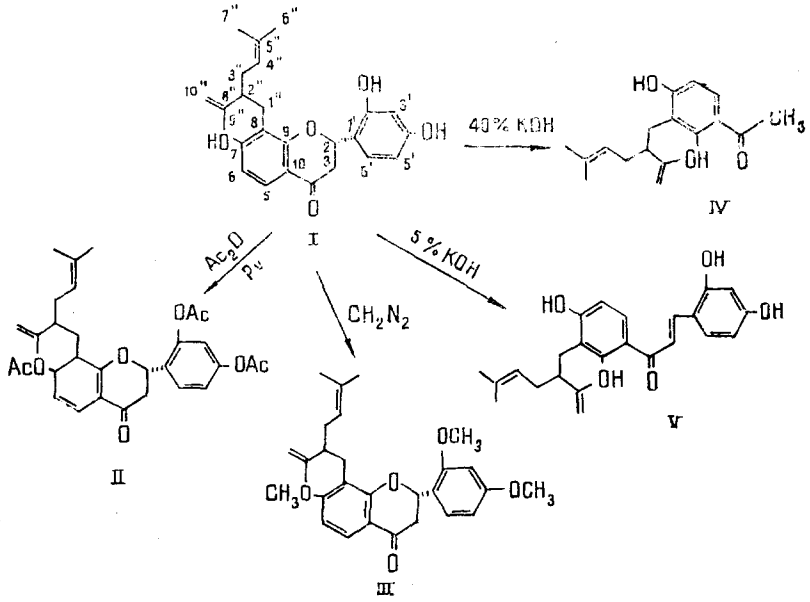
group indicate that the (I) molecule does not contain an hydroxy group at C-5 [4, 6]. Two one-proton doublets at 7.95 and 6.77 ppm with J = 8.5 Hz showing ortho-coupling in the PMR spectrum of (I) obviously belong to the H-5 and H-6 protons, respectively.

A comparative analysis of the PMR and ^{13}C NMR spectra of vexibinol [8], of kushenols A, E, and F [9, 10] and of lavandulyl alcohol (2-isoprenyl-5-methylhex-4-enol) [11] with those of lehmannin showed that the molecule of the latter contained a lavandulyl side chain. The presence in the mass spectrum of (I) of the peaks of ions with m/z 285 [$M^+ - 123$ (C_9H_{15})], m/z 267 [$M^+ - H_2O - C_9H_{15}$] and m/z 124 $[C_9H_{16}]^+$ also confirmed our hypothesis [8, 9].



Scheme 1

In the mass spectra of compounds (I) and (III) there are the peaks of ions with m/z 136 and 164, respectively, formed as the result of the retrodiene decomposition of the flavanone nucleus [12]. These fragments indicate that there are two phenolic hydroxyls in ring B of compound (I) and, consequently, the lavandulyl group is located in ring A. A comparative study of the UV spectra of compound (I) taken in ethanol with the addition of sodium acetate established the presence of a phenolic hydroxy group at C-7 [4].

The interaction of lehmannin with concentrated caustic potash solution in an atmosphere of nitrogen led to the cleavage of the flavanone nucleus with the formation of compound (IV), identical with 2,4-dihydroxy-3-(2'-isopropenyl-5'-methylhex-4'-enyl)acetophenone which we had obtained previously from ammothamnidin [3]. This permitted an unambiguous determination of the location of the lavandulyl side chain at C-8. As was shown above, two of the three hydroxy groups in the (I) molecule are located in ring B. In the PMR spectra of compounds (I)-(III), the three aromatic protons give a pattern corresponding to an ABX spin system with the signal of the X (H-6') proton, present in the weakest field, having an ortho-coupling constant of 8.5 Hz. This shows the presence of substituents [OH groups in compound (I)] in the C-2' and C-4' positions.

The circular dichroism spectrum of lehmannin showed a positive maximum at 338 nm ($\Delta\varepsilon$ = +5.35) and a negative one at 305 nm ($\Delta\varepsilon$ = −10.0). Consequently, lehmannin has the 2S absolute configuration [13].

Thus, lehmannin has the structure of 2',4',7-trihydroxy-8-(2"-isopropenyl-5"-methylhex-4"-enyl)flavanone (I).

The ^{13}C NMR spectrum of compound (I) agrees well with its structure. The resonance signals were identified by studying the spectra taken under the conditions of complete and partial suppression of spin-spin coupling with protons, by a comparative analysis of the values of the chemical shifts of monotypical carbon atoms of the molecules of vexibinol [8]. Kushenols E and F [10], isobavachin (4',7-dihydroxy-8-prenylflavanone) [14], and lehmannin, and also of other literature information [6].

Table 1 gives the values of the chemical shifts, multiplicities, and assignments of the signals in the ^{13}C NMR spectrum of lehmannin.

TABLE 1. Chemical Shifts of the Carbon Atoms of Lehmannin in DMSO-d_6 (δ, ppm, 0 – TMS)

C-atom	δ, ppm	C-atom	δ, ppm	C-atom	δ, ppm
2	75,0 d	1′	117,2* s	4″	123,7 d
3	43,2 t	2′	155,7 s	5″	131,5 s
4	192,6 s	3′	103,0 d	6″	17,9 q
5	126,1* d	4′	158,6 s	7″	25,9 q
6	110,2 d	5′	107,0 d	8″	148,4 s
7	163,0* s	6′	128,1* d	9″	19,1 q
8	113,9 s	1″	27,6 t	10″	111,3 t
9	162,5* s	2″	46,7 d		
10	115,3* s	3″	31,4 t		

*Assignment of the chemical shifts ambiguous.

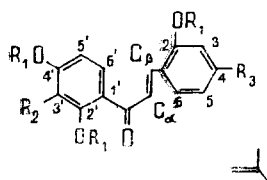
TABLE 2. Values of the Chemical Shifts of the Signal of C-2 Carbon Atom in the ^{13}C NMR Spectra of Flavanones

Flavanones containing an OH or OCH_3 group at C-2′	δ, ppm	Flavanones unsubstituted in the C-2′ position	δ, ppm
2-Hydroxy-7-methoxyflavonone [16]	74,9	7-Methoxyflavonone [16]	79,7
		5,7-Dihydroxyflavanone [6]	78,4
2′,7-Dimethoxyflavonone [16]	75,1	4′,7-Dihydroxyflavonoe [16]	79,5
Euchrestaflavonone B [17]	74,1	3′-Hydroxy-7-methoxyflavonone [16]	79,3
Cudraflavonone A [18]	73,6		
Vexibinol [8]	73,7	Isobavachin [14]	78,8
Vexibidin [8]	73,4	Sophoraflavone B [14]	78,3
Kushenol A [9]	75,5	Flemiflavanone D [20]	79,2
Cuwanone D [19]	75,3	Amoradin [21]	78,4
Kushenol E [10]	75,4	Nymphaeol A [22]	79,5
Lehmmanin	75,0	Euchrestaflavone A [23]	78,5

A comparative study of the ^{13}C NMR spectra of the flavanones showed that compounds containing substituents (OH and OCH_3) in the C-2′ position can be distinguished by means of the value of the chemical shift of the C-2 carbon atom. In flavanones having no substituents in the C-2′ position, the signal of the C-2 carbon resonates in the range of 78.3-79.5 ppm (Table 2). The presence of an OH or an OCH_3 group at C-2′ leads to an upfield shift of the C-2 signal by 4.0-5.0 ppm. This characteristic upfield shift of the signal of the C-2 carbon atom in a C-2′–OH or –OCH_3-substituted flavanone is apparently due mainly to the spatial effect of the oxygen of the OH or OCH_3 group on the C-2 carbon atom.

An analogous upfield shift of the CH_3 carbon atom ($\Delta\delta = -4.6$ ppm) is also observed in the ^{13}C NMR spectrum of ortho-cresol as compared with that of toluene ([15], see Table 4.49). It must be mentioned that the effect of the conjugation of the OH group is insignificant, since in para-cresol this magnitude is extremely small, amounting to only 0.7 ppm. Thus, from the value of the chemical shift of the signal of the C-2 carbon atom of flavanone it is possible to judge whether an OH or OCH_3 group is present in the C-2′ position.

It is known that flavanones readily isomerize in an alkaline medium to the corresponding chalcones [24]. Under the action of an ethanolic solution of caustic potash, lehmannin was converted into the chalcone (Va), which proved to be identical with ammothamnidin [3]. Previously, on the basis of spectral characteristics and some chemical transformations, structure (Vb) with three phenolic hydroxy groups was proposed for ammothamnidin [3].

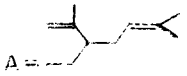


Va. $R_1 = H$, $R_2 = A$, $R_3 = OH$

Vb. $R_1 = R_3 = H$, $R_2 = A$

VIc. $R_1 = COCH_3$, $R_2 = A$, $R_3 = OCOCH_3$

VII. $R_1 = H$, $R_2 = B$, $R_3 = OH$



Scheme 2

TABLE 3. ^{13}C Chemical Shifts (δ, ppm, 0 – TMS, DMSO-d_6) and Assignment of the Signals of the Carbon Atoms of Ammothamnidin (V) and of Morachalcone A (VII)

C atom	V	VII [25]	C atom	V	VII	C atom	V
1 s	113,5*	113,3	1′ s	112,6	112,7	4″ d	123,4
2 s	159,2	159,2	2′ s	164,1	163,4	5″ s	130,5
3 d	102,5	102,4	3′ s	113,9*	114,4	6″ q	17,6
4 s	161,5*	161,5	4′ s	162,5*	161,9	7″ q	25,5
5 d	108,0*	108,0	5′ d	107,0*	107,2	8″ s	147,7
6 d	130,5	130,4	6′ d	129,3	129,6	9″ q	18,5
C-α d	115,7	115,6	1″ t	26,9		10″ t	110,7
C-β d	139,7	139,7	2″ d	46,0			
C=O s	191,0	191,9	3″ t	30,9			

*Assignment of the chemical shifts ambiguous. For morachalcone A only the signals of the carbon atoms of the chalcone nucleus are given.

An analysis of ^{13}C NMR spectra showed that in the weak-field region, in addition to the signal of the C=O group, the signals of four aromatic carbon atoms bearing hydroxy functions appeared at 159.2, 161.5, 162.5, and 164.1 ppm. On this basis, ammothamnidin must contain four, and not three, phenolic hydroxy groups. In actual fact, the integral intensity of the signals of the protons of the methyl radicals of Ar–$OCOCH_3$ groups (δ 2.21-2.26 ppm) in the PMR spectrum of ammothamnidin acetate (VI) is equal to 12 protons, which corresponds to four acetoxy groups. This was also confirmed by the presence in its mass spectrum of a weak peak of the molecular ion with m/z 576. Consequently, the ammothamnidin molecule contains five oxygen atoms and must have a molecular weight of 408 amu. However, its mass spectrum lacked the peak of the M^+ ions, and in the high-mass region the peak of an ion with m/z 392 was observed which, as we have now found, was previously taken as the peak of the molecular ion. By an accurate mass measurement, its composition was determined as $C_{25}H_{28}O_4$ [3]. This ion is obviously formed from an unstable molecular ion as the result of the ejection of atomic oxygen. The peak of the M – 16 ion is also present in the spectrum of lehmannin.

The splitting out of atomic oxygen from the molecule under the conditions of mass spectrometry is also characteristic for flemiflavanone D, and this was the main cause of the erroneous treatment in the choice of a structure which was then corrected [20].

In the ^{13}C NMR spectrum of (V) with off-resonance incomplete suppression of spin-spin coupling with protons, 10 of 25 carbon signals were represented by singlets, nine by doublets, three by triplets, and another three by quartets. The assignment of the signals of the basic chalcone nucleus was made by a mutual comparison of the ^{13}C NMR spectra of chalcones close in structure [6, 7]: morachalcone A (VII) [25] and ammothamnidin (Table 3). The values of the chemical shifts of the signals of the ^{13}C nuclei of the main skeleton of ammothamnidin agree well with those of morachalcone A (VII) which differs from the former only by the structure of the side chain at C-3'.

On the basis of the facts given above, ammothamnidin has the structure of 2,2',4,4'-tetrahydroxy-3'-(2"-isopropenyl-5"-methylhex-4"-enyl)chalcone (V).

Thus, from the roots of the dye plant Ammothamnus lehmannii the flavanone lehmannin and the chalcone corresponding to it, ammothamnidin, have been isolated. Both compounds give an intense orange coloration under the action of aqueous solutions of soda and of alkalies. Consequently, the tinctorial properties of the roots are explained by the presence of ammothamnidin and lehmannin which make up the bulk of the tinctorial substances.

Previously, G. V. Lazur'evskii isolated resorcinol and β-resorcylic acid from the product of the alkaline fusion of the total pigments of this plant (soforeol), and by distillation over zinc dust in a current of hydrogen he also obtained 2,6-dimethylheptadiene [2]. The origin of these substances has become clear with the determination of the structures of compounds (I) and (V).

EXPERIMENTAL

General observations. Thin-layer chromatography (TLC) was performed on Silufol plates. On TLC, the flavonoids were detected by spraying with vanillin–sulfuric acid [5]. For

column chromatography we used type L silica gel (Czechoslovakia) with a grain size of 150 μ, and polyamide with a particle size of <250 μ. The following solvent systems were used: 1) chloroform–hexane: 1) (3:1); b) (4:1); and c) (9:1); 2) chloroform–ethanol: a) (19:1); b) (9:1); and c) (17:3); and 3) hexane–acetone (1:1).

Mass spectra were obtained on a MKh-1310 instrument, IR spectra on a UR-20 spectrophotometer, UV spectra on a Hitachi EPS-3 instrument in ethanol, and NMR spectra (^1H and ^{13}C) on a Tesla BS-567 A spectrometer (Czechoslovakia) at working frequencies of 100.03 and 25.14 MHz in Py-d_5 and DMSO-d_6, respectively.

The chemical shifts of the carbon atoms were calculated relative to the signals of the solvent DMSO-d_6 ($\delta_{TMS} = \delta_{DMSO\text{-}d_6} + 39.6$ ppm). The circular dichroism spectrum was recorded on a Jasco J-20 spectropolarimeter.

Isolation of Lehmannin (I) and of Ammothamnidin (V). The dried and comminuted roots (1.2 kg) of Ammothamnus lehmannii gathered in May, 1984, were exhaustively extracted with chloroform at room temperature. The solvent was distilled off, giving 96.0 g of thick extract. Part of the dried extract (50.0 g) was chromatographed on a column of silica gel (800 g) with elution first by system (1a) and then (1c). On elution with system (1c), 21.0 g of a mixture of ammothamnidin and lehmannin was obtained which was rechromatographed on a column of polyamide sorbent (227 g). Elution by systems 1a and 1c gave 2.74 g of ammothamnidin and 5.6 g of technical lehmannin. The lehmannin was purified by rechromatography on a column of polyamide (with elution by systems 2a, 2b, and 2c). Fractions containing chromatographically homogeneous lehmannin were collected (4.13 g).

The total yield calculated on the weight of the air-dried raw material amounted to 0.23% for ammothamnidin and 0.34% for lehmannin.

Lehmannin (I) $C_{25}H_{28}O_5$, mp 102-103°C, $[\alpha]_D$–63.7° (c 0.43; methanol); λ_{max}^{EtOH} 242, 288, 313 nm (log ε 4.06, 4.09, 3.81); +CH_3COONa 287, 315 nm; +CH_3COONa/H_3BO_3 286, 314 nm; +$AlCl_3$ 287, 315 nm; +$AlCl_3$/HCl 286, 313 nm. ν_{max}^{KBr}, cm^{-1}: 3270-3110, 1648, 1605, 1590, 1540, 1520, 980, 875, 850, 830.

PMR spectrum (C_5D_5N; δ, ppm: 0 – HMDS) 1.42, 1.46, 1.75 (3 H each, br. s, 3 × CH_3–C=), 2.26 (2H, m, H-3"), 2.88-3.28 (5H, m, 2H-3, H-1", H-2"), 4.69 and 4.80 (1H each, br. s, 2H-10"), 5.15 (1H, m, H-4"), 6.13 (1H, dd, J = 11.0 and 5.0 Hz, H-2), 6.77 (d, J = 8.5 Hz, H-6), 6.79 (dd J = 9.0 and 2.5 Hz, H-5'), 6.82 (br. s, H-3'), 7.68 (1H, d, J = 9.0 Hz, H-6'), 7.95 (1H, d, J = 8.5 Hz, H-5). For the ^{13}C NMR spectrum, see Table 1.

Mass spectrum, m/z (%): M^+ 408 (4.5), 393 (13), 392 (M – 16) (48.5), 391 (13), 390 (8), 377 (2), 349 (3), 325 (24), 285 (M – 123) (2.5), 270 (15), 269 (42), 268 (35.5), 267 (40), 266 (8), 203 (16.5), 149 (22.5), 136 (4), 124 (55), 123 (27.5), 109 (55), 86 (26), 85 (19.5), 84 (100). CD spectrum (c 0.147; ethanol): $\Delta\varepsilon$ = +20.1 (223 nm), $\Delta\varepsilon$ = –1.0 (247 nm), $\Delta\varepsilon$ = –10.0 (305 nm), $\Delta\varepsilon$ = +5.35 (338 nm).

Lehmannin Triacetate (II). With heating in the water bath, 53 mg of lehmannin was dissolved in 1.5 ml of anhydrous pyridine, and then 2.5 ml of acetic anhydride was added and heating was continued for another 1 h. The reaction mixture was diluted with water and was extracted exhaustively with chloroform. The combined chloroform extracts were washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness.

This gave 42 mg of the amorphous vitreous triacetate (II), $C_{31}H_{34}O_8$, ν_{max}^{film}, cm^{-1}: 1798, 1720 (ester groups), 1669 (C=O of a γ-pyrone), 1621, 1523 (aromatic C=C bonds), 1452, 1387, 1310, 1225-1220, 982, 825, 764.

PMR spectrum ($CDCl_3$; δ, ppm: 0 – HMDS): 1.43 (3H, s, CH_3–C=), 1.54 (6H, s, 2 × CH_3–C=), 2.18; 2.21; 2.23 (3H, s, each, 3 × CH_3COO), 2.42-2.95 (4H, m, 2H-3, H-1"), 4.41 and 4.55 (each 1H, br. s, 2H-10"), 4.90 (1H, m, H-4"), 5.48 (1H, dd, J = 11.0 and 5.55 Hz, H-2), 6.72 (1H, d, J = 8.5 Hz, H-6), 6.97 (1H, br. s, H-3'), 7.05 (1H, dd, J = 2.5 and 8.0 Hz, H-5'), 7.64 (1H, d, J = 8.0 Hz, H-6'), 7.77 (1H, d, J = 8.5 Hz, H-5).

Triethyl Ether of Lehmannin (III). An ethereal solution of diazomethane was added to a solution of 200 mg of lehmannin in 1.5 ml of anhydrous methanol, and the mixture was left in the refrigerator. After a day, the solvent was distilled off and the residue was chromatographed on a column of silica gel. Elution with system (1b) yielded the oily trimethyl ether (III), $C_{28}H_{34}O_5$, ν_{max}^{film}, cm^{-1}: 1687 (C=O of a γ-pyrone), 1600, 1515 (aromatic C=C bonds), 840, 808. λ_{max}^{EtOH}, 283, 312* nm.

PMR spectrum ($CDCl_3$; δ, ppm; 0 – HMDS): 1.43; 1.54; 1.60 (3H, s, each, 3 × CH_3–C=), 1.95 (2H, m, H-3"), 2.57-2.86 (4H, m, H-3, H-1"), 3.73; 3.76; 3.79 (3H, s, each, 3 × CH_3O), 4.43 and 4.54 (1H, m, each, 2H-10"), 4.93 (1H, m, H-4"), 5.61 (1H, dd, J = 10.5 and 6.0 Hz, H-2), 6.42 (1H, d, J = 2.2 Hz, H-3'), 6.51 (1H, dd, J = 2.2 and 8.5 Hz, H-5'), 6.64 (1H, d, J = 9 Hz, H-6), 7.46 (1H, d, J = 8.5 Hz, H-6'), 7.77 (1H, d, J = 9 Hz, H-5).

Mass spectrum, m/z (%): M^+ 450 (60), 419 (M – OCH_3) (4), 407 (M – CO–CH_3) (3), 381 (M – C_5H_9) (10.5), 327 (M – C_9H_{15}) (100), 287 (11.5), 286 (35), 217 (55), 191 (5), 179 (5.5), 164 (35), 163 (75), 141 (14.5), 139 (14), 137 (14), 123 (5.5), 121 (8.5), 105 (6).

Alkaline Cleavage of Lehmannin. A solution of 310 mg of lehmannin in 40 ml of 40% aqueous caustic potash was treated in the water bath under reflux in an atmosphere of nitrogen for 3 h. The reaction mixture was acidified with 15% hydrochloric acid and was extracted with ether (5 × 60 ml). The combined ethereal extracts were washed with sodium hydrogen carbonate solution and then with water and were evaporated to dryness. The residue was chromatographed on a column of silica gel in system 1b. This gave 57 mg of substance (IV), $C_{18}H_{24}O_3$, mp < 60°C, M^+ 288, λ_{max}^{EtOH}, 218, 234*, 320 nm [3].

Ammothamnidin (V) from Lehmannin (I). A solution of lehmannin (60 mg) in 10 ml of 5% ethanolic caustic potash was kept at room temperature for 20 h. Then the reaction mixture was heated at 50-60°C for 30 min, was diluted with water, and after the residual ethanol had been distilled off in vacuum, it was acidified with 10% hydrochloric acid and extracted with ether. The combined ethereal extracts were washed with water and evaporated to dryness. The residue was chromatographed on a column of silica gel in system 3. After recrystallization of the main reaction product from benzene, 39 mg of compound (V) was obtained with mp 113-114°C, $[\alpha]_D$ + 4.5° (c 0.22; methanol), identical with ammothamnidin.

UV spectrum: λ_{max}^{EtOH} 232*, 261*, 320*, 390 nm (log ε 4.20, 4.01, 4.03, 4.48), + CH_3COONa 398 nm; + CH_3COONa/H_3BO_3 394 nm. PMR spectrum (assignment of the signals reconsidered; C_5D_5N; δ, ppm; 0 – HMDS): 1.45; 1.50; 1.80 (3H, s, each, 3 × CH_3–C=), 2.28 (2H, m, H-3"), 3.80 (3H, m, H-1", H-2"), 4.65 and 4.75 (1H, br. s, each, 2H-10"), 5.13 (1H, m, H-4"), 6.38-6.72 (3H, m, H-3, H-5, H-5'), 7.64 (1H, d, J = 8.0 Hz, H-6), 7.87 (1H, d, J = 9.0 Hz, H-6'), 8.00 (1H, d, J = 16 Hz, H_α), 8.69 (1H, d, J = 16 Hz, H_β).

Ammothamnidin Tetraacetate (VI). Ammothamnidin (85 mg) was acetylated with acetic anhydride (3 ml) in pyridine (2 ml) at room temperature for 24 h. Then the reaction mixture was poured into water and the precipitate that deposited was filtered off. This gave 67 mg of the tetraacetate (VI), $C_{33}H_{36}O_9$, mp < 70°C, $\nu_{max}^{CHCl_3}$, cm^{-1}: 1773 (ester C=O), 1642 (chalcone C=O), 1602, 1583, 1500 (C=C), 1258, 1203, 981, 905, 765.

Mass spectrum, m/z (%): M^+ 576 (0.3), 534 (6), 492 (6), 491 (7), 475 (6.3), 449 (5), 423 (6.7), 407 (8), 369 (33), 352 (11), 327 (8.3), 321 (10), 310 (15), 309 (15), 268 (18), 267 (25), 245 (15), 203 (48), 165 (10), 163 (9), 161 (13), 149 (100), 137 (23), 123 (68), 111 (32).

CONCLUSION

1. The new flavanone lehmannin has been isolated from the roots of Ammothamnus lehmanni Bunge (family Fabaceae); it has the structure of 2',4',7-trihydroxy-8-(2"-isopropenyl-5"-methylhex-4"-enyl)flavanone.

2. On the basis of a comparative study of the ^{13}C NMR spectra of a number of flavanones, an empirical rule has been found which permits the presence or absence of substituents (OH and OCH_3) at C-2' to be predicted from the value of the chemical shift of the C-2 carbon signal.

3. The structure previously proposed for ammothamnidin has been corrected. It has been established that it has the structure of 2,2',4,4'-tetrahydroxy-3'-(2"-isopropenyl-5"-methylhex-4"-enyl)chalcone. The assignment of the signals in the ^{13}C NMR spectrum of this calcone has been reconsidered.

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