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ISOPRENOIDS OF *Bryonia*.
I. PENTACYCLIC TRITERPENES AND STEROL OF *Bryonia melanocarpa*

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The isoprenoid composition of Bryonia melanocarpa *Nab. (Cucurbitaceae) has been studied. Eight components of the roots of this plant have been identified — two pentacyclic triterpenoids: isomultiflorenol (1) and bryonolic acid (4); three phytosterols: (24R)-24-ethyl-5α-cholest-7-en-3β-ol (7), stigmasta-7E,24(28)-dien-3β-ol (9), and 4α-methylstigmasta-7E,24(28)-dien-3β-ol (11); three sterol glycosides: (24R)-24-ethyl-5α-cholest-7-en-3β-ol 3-O-β-D-glucopyranoside (8), stigmasta-7E,24(28)-dien-3β-ol 3-O-β-D-glucopyranoside (10), and 4α-methylstigma-7E,24(28)-dien-3β-ol 3-O-β-D-glucopyranoside (12).*

Plants of the genus *Bryonia* (bryony), fam. Cucurbitaceae, are not numerous. In the flora of the USSR [1] five species of this genus are described: *B. alba* L., *B. transoxana* Vass., *B. dioica* Jacq., *B. monoica* Aitsch et Hemsl, and *B. Lappifolia* Vass. The first three of these plants are found in Central Asia and one more: the — to all appearance — endemic species *B. melanocarpa* Nab. [2, 3]. Some of these plants (*B. alba* and *B. dioica*) are ancient medicinal plants [4] and, in view of this, have been fairly well studied in the chemical respect [5]. At the same time, there are no reports on any chemical study of *Bryonia melanocarpa*. On the other hand, a dry powder obtained from the roots of *B. melanocarpa* is used in veterinary medicine for the treatment of all possible wounds in animals [2, 3]. In view of this, we have studied the roots of *B. melanocarpa* for the presence of various groups of isoprenoids. In a methanolic extract of the roots of *B. melanocarpa*, in addition to cucurbitacins, we detected pentacyclic triterpenoids and sterols. These two groups of compounds are the subject of the present paper.

From the feebly polar fraction of a methanolic extract of *B. melanocarpa* we obtained four chromatographically homogeneous crystalline products of triterpene and sterol natures, designated in order of increasing polarity as substances (**1-4**).

According to its ^1H and ^{13}C NMR spectra (Tables 1 and 2), substance (**1**)(1), composition $C_{30}H_{50}O$, was a pentacyclic triterpenoid containing one secondary hydroxy group and one tetrasubstituted double bond. The singlet nature of the signals of the methyl groups in the PMR spectrum of triterpenoid (1) showed that the substance under consideration did not belong to the ursane series, while in an oleanane only one position is possible for a tetrasubstituted double bond: C-13−C-18. The appearance of the maximum peak of an ion with *m/z* 259 ($C_{18}H_{27}O$) in the mass-spectrometric fragmentation of isoprenoid (1) presupposed the cleavage of ring *D* at the C-13−C-18 and C-14−C-15 bonds, which, in its turn, also excluded an olean-13(18)-ene skeleton. Such fragmentation is possible in the series of pentacyclic triterpenoids containing a double bond in the 7-, 8-, or 9(11)- position [6, 7]. In particular, on mass fragmentation under electron impact, multiflorenol derivatives form analogous ions.

The isomerization of multiflorenol leads to the migration of the double bond into position 8 and to the formation of isomultiflorenol, the double bond in which is tetrasubstituted [8].

The Jones oxidation of compound (1) gave the ketone (3). The ORD curve of the latter coincided with that of isomultiflorenone, showing the presence of 3-oxo-and Δ^8- functions [8]. The physicochemical constants and other spectral characteristics of ketone (3) also coincided with the analogous parameters of isomultiflorenone [8], obtained by the oxidation of isomultiflorenol and later isolated from *Cucurbita lundelliana* [10].

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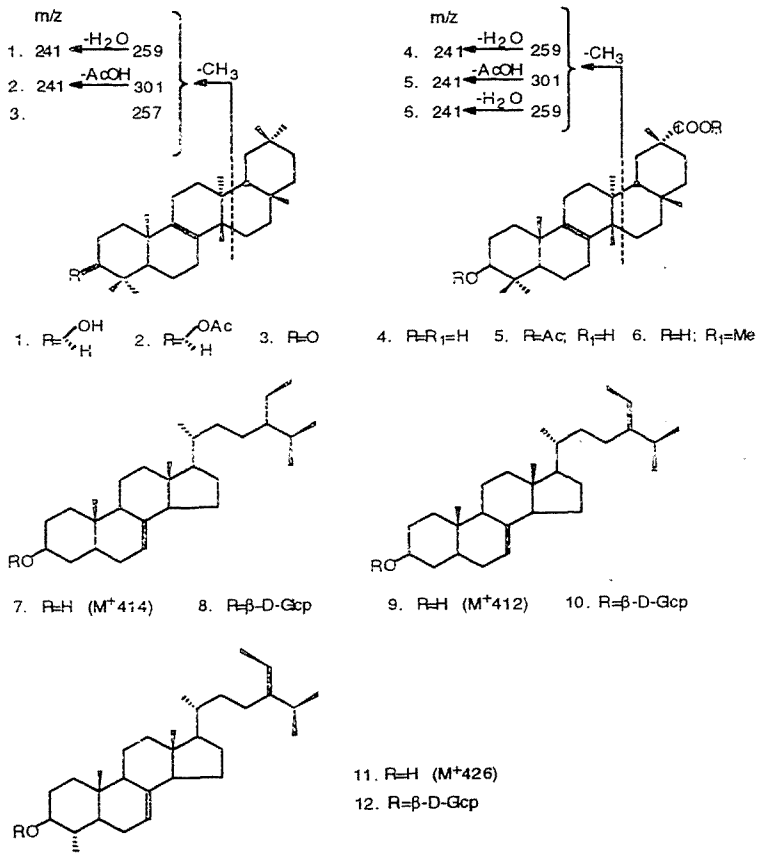

Compound (1) formed a monoacetate (2). A consideration of the PMR spectra of compounds (1) and (2) and also the ^{13}C NMR spectrum of triterpenoid (1) enabled us to draw the conclusion that compound (1) contained a 3β-hydroxy group. Consequently, the structure of triterpenoid (1) corresponded to that of isomultiflorenol. The identity of compound (1) and isomultiflorenol was confirmed by the good agreement of the physicochemical constants of the substances and their acetates.

Thus, triterpenoid (1) was isomultiflorenol, which was first obtained by the isomerization of multiflorenol [8] and was later isolated from *Euphorbia supina* [11].

Analysis of the mass and ^1H and ^{13}C NMR spectra of substance (**3**) (4) with the composition $C_{30}H_{48}O_3$ enabled us to assign this compound, as well to the multiflorenol series. The presence in the ^{13}C NMR spectrum of triterpenoid (4) of two singlet signals of sp^2-hybridized carbon atoms at 134.60 and 134.20 ppm due to a tetrasubstituted π-bond showed that the substance under consideration belonged to the iso- series.

In its IR spectrum, triterpenoid (4) showed absorptions characteristic for hydroxy and carbonyl groups (3460 and 1685 cm^{-1}, respectively). The formation of the methyl ester (6) on the methylation of triterpenoid (4) with diazomethane showed that the band at 1685 cm^{-1} was due to the carbonyl of a carboxyl group. Taking into account the indices of the PMR spectra of substances (4-6), the formation of the monoacetate (5) by the acetylation of compound (4) with acetic anhydride in pyridine indicated that the third oxygen atom was in a secondary hydroxy group. As was to be expected, in the ^{13}C NMR spectrum of triterpenoid (4) resonance signals were observed from a secondary carbonyl carbon and a carboxyl carbon, at 78.00 and 181.20 ppm, respectively. The chemical shift of the carbon atom of the secondary hydroxy group determined the 3β-position of the latter. The parameters of the resonance signal of the proton geminal to the hydroxy group agreed well with this conclusion.

In the mass spectrum of triterpenoid (4), as in that of isomultiflorenol (1) the maximum peak of an ion with *m/z* 259 was observed. This fact demonstrated the localization of the carboxyl group in ring *E*. A comparative study of the ^{13}C NMR spectra of isomultiflorenol and of the monohydroxy monocarboxylic acid (4) revealed a considerable change in the chemical shifts of carbon atoms 19-21 on passing from (1) to (4) and also the absence of a signal from a 29-CH_3 group. The magnitudes and signs of the chemical shifts of carbon atoms 20, and 19 and 21, are well inscribed within the β- and γ- contributions, respectively, of the carbonyl oxygen of the carboxyl function, which must include the C-29 atom.

TABLE 1. Chemical Shifts (δ, ppm), Multiplicities, and SSCCs (J, Hz) of the Protons of Compounds (1-6)

Compound	Positions of the protons		
	H–3	CH_3 groups	OAc, OCH_3
1	3.47 dd (10; 6)	0.99; 1.02; 1.03; 1.06; 1.07; 1.07; 1.12; 1.25	–
	[3.10 dd (10;6)]	[0.74;0.91; 0.91; 0.91; 0.94; 0.95; 1.00; 1.01]	–
2	[4.44 dd (12; 5)]	[0.82; 0.82; 0.92; 0.92; 0.92; 0.92; 0.99; 1.01]	[1.98]
3	–	[0.90; 0.90; 0.92; 0.99; 0.99; 1.02; 1.02; 1.03]	–
4	3.36 dd (10; 6)	0.98; 1.03; 1.05; 1.08; 1.19; 1.26; 1.40	–
5	4.46 dd (10; 6)	0.77; 0.77; 0.81; 0.91; 0.97; 1.12; 1.30	1.92
	[4.44 dd (10; 6)]	[0.82; 0.82; 0.82; 0.92; 0.92; 1.00; 1.19]	[1.99]
6	3.33 dd (10; 6)	0.82; 0.90; 0.90; 0.90; 0.94; 1.11; 1.13	3.56
	[3.18 dd (10; 5)]	[0.69; 0.73; 0.89; 0.89; 0.94; 0.97; 1.12]	[3.56]

*The spectra were taken in deuterochloroform and deuteropyridine. The indices given in square brackets were obtained in deuterochloroform. The spectra of compounds (1) and (4), taken in deuteropyridine, were recorded on a Bruker AM-400 instrument with TMS as internal standard. The other spectra were obtained on a Tesla BS 567 A instrument with HMDS as internal standard. The signals of the methyl groups were singlets.

TABLE 2. Chemical Shifts of the Carbon Atoms of Compounds (1) and (4) (δ, ppm, C_5D_5N, 0 — TMS)

C atom	Compound		C atom	Compound	
	1	4		1	4
1	34.52	35.10	16	35.62	35.54
2	26.46	25.51	17	30.00	31.31
3	78.10	78.00	18	44.43	45.20
4	38.20	37.85	19	34.56	31.16
5	51.21	50.96	20	28.46	40.60*
6	21.18	21.08	21	36.95	30.53
7	27.90	27.98	22	37.02	37.53
8	135.10	134.60	23	28.71	28.62
9	134.20	134.20	24	16.60	16.50
10	37.60	37.71	25	19.28	17.99
11	19.68	19.64	26	24.81	22.40
12	30.95	30.70	27	20.13	20.15
13	41.40	42.15*	28	31.65	31.46
14	39.50	39.41	29	34.77	181.20
15	28.85	28.74	30	33.03	33.33

*The assignment of the signals marked with asterisks is uncertain.

Consequently, triterpenoid (4) was 3β-hydroxymultiflor-8-en-29-oic acid. An identical structure has been ascribed to bryonolic acid, isolated from *Bryonia dioica* Jacq. [12]. The triterpene acid (4), the monoacetate (5), and the methyl ester (6) also agreed with bryonolic acid and its corresponding derivatives in terms of physicochemical constants.

From its high-resolution electron-impact mass spectrum, substance (**2**) consisted of a mixture of three sterols, with M^+ 426 (11), 414 (7), and 412 (9). In the PMR spectrum ($CDCl_3$, TMS) of the mixture of sterols, the 18- and 19-methyl groups resonated at 0.56 and 0.80 ppm, respectively, and showed the presence of a double bond at C-7 [13]. In the PMR spectrum of β-sitoterol taken under analogous conditions the signals of the methyl groups under consideration are observed at 0.68 and 1.00 ppm. As was to be expected, the IR spectrum of the mixture of ketones obtained by the Jones oxidation [2] of substance (**2**) had an absorption band at 1715 cm^{-1}, showing the absence of conjugation with the double bond.

It followed from the molecular masses of the phytosterols and in the light of the ^1H and ^{13}C NMR spectra that one of them was a 24-ethyl derivative (M^+ 414), while the other two were 24-ethylidene derivatives. The sterol with M^+ 426 contained a 4α-methyl group, in addition.

In the PMR spectrum of substance (**2**) the H-25 signal was not observed in the 2.5-3.0 ppm range and, to all appearance, was shifted upfield, beginning from the methylene hump. This fact permits the conclusion of the E- configuration of the C-24-C-28 double bond [14] where it is present.

In the ^{13}C NMR spectrum of substance (**2**) taken in deuterochloroform the signal from C-24 of the sterol (7) molecule was observed at 45.80 ppm. This fact unambiguously determined the R-configuration of the C-24 chiral center [15]. Consequently, sterol (7) was (24R)-24-ethyl-5α-cholest-7-en-3β-ol, i.e., scottenol. Sterol (9) was stigmasta-7E,24(28)-dien-3β-ol, and sterol (11) 4α-methylstigmasta-7E,24(28)-dien-3β-ol. The GLC analysis of substance (**2**) in various phases showed that sterol (7) predominated in the mixture (more than 50%). Sterols (7) and (9) have been isolated from *Bryonia dioica* [16].

The chromatographically homogeneous substance (**4**) had a glycosidic nature and, according to GLC [17], contained one molecule of *D*-glucose. The Smith degradation [18] of substance (**4**) gave a genin consisting of three components — (7), (9), and (11) — in approximately the same ratio as in substance (**2**).

In the PMR spectrum of substance (**4**) the anomeric proton of the *D*-glucose residue gave a signal at 4.90 ppm in the form of a doublet with the SSCC 8 Hz, showing the β-configuration, the $^4C_1$-conformation, and, consequently, the pyranose form of the monosaccharide residue [19].

Thus, substance (**4**) was a mixture of glycosides (8), (10), and (12) — the β-*D*-glucopyranosides of phytosterols (7), (9), and (11), respectively.

EXPERIMENTAL

For general observations, see [20]. The following solvent systems were used: 1) chloroform–methanol (15:1); 2) hexane–benzene (1:1).

The GLC analysis of the sterols was conducted on a Chrom-5 chromatograph. Column 3 mm × 2.5 m with the phases 5% of SKTFT-50X silicone rubber and 10% of SE-30 on Chromaton N-AW-DMCS. The carrier gas was helium at the rate of 30 ml/min. The temperature of the evaporator was 300°C, and that of the detector 270°C.

PMR spectra were recorded on Tesla BS 567A and Bruker AM-400 instruments in deuteropyridine or deuterochloroform. ^{13}C NMR spectra were obtained on a Bruker AM-400 instrument. J-Modulation spectra were used to interpret the ^{13}C NMR spectra.

Isolation and Separation of the Isoprenoids of *Bryonia melanocarpa*. The air-dry comminuted roots (12.85 kg) of *Bryonia melanocarpa* collected on September 17, 1985, in the environs of kolodets Bimirza, Chardara region of Chimkent province, Republic of Kazakhstan, were exhaustively extracted with methanol (60 liters). The methanolic extract was evaporated to dryness, giving 780 g of extractive substances. The dry extract (435 g) was homogenized with an equal amount of KSK silica gel and was deposited on a column of the same silica gel. Elution of the column successively with chloroform and system 1 yielded fractions 1-4, containing chromatographically homogeneous crystalline compounds, which were designated as substances (**1**)-(**4**), respectively. The yield of substance (**1**) was 210 mg (0.0029%; here and below the yields are given on the air-dry raw material); substance (**2**) 800 mg (0.0111%); substance (**3**) 480 mg (0.0066%)), and substance (**4**) 500 mg (0.0069%).

Isomultiflorenol (1) — Substance (1), $C_{30}H_{50}O$, mp 180-181°C (from $CHCl_3$–MeOH, 1:1), $[\alpha]_D^{22}$ +32.5±2° (*c* 0.8; $CHCl_3$). Literature: 181-182° (from Me_2CO), $[\alpha]_D$ + 28° ($CHCl_3$) [8]; mp 185-187° (from $CHCl_3$–MeOH), $[\alpha]_D^{23}$ + 27.9° (*c* 0.97; $CHCl_3$) [11]. IR spectrum (KBr, v, cm^{-1}): 3510 (OH). Mass spectrum, *m/z* (%): M^+ 426 (61.5), 411 (46.2), 393 (7.7), 328 (3.2), 259 (100), 247 (61.5), 241 (53.8), 229 (61.5), 218 (100), 205 (84.6), 203 (46.2), 191 (38.5), 189 (30.8). For the ^1H and ^{13}C NMR spectra, see Tables 1 and 2.

The Mixture of Sterols (7), (9), and (11) — Substance (2). In the mass spectrum of substance (**2**) we observed the peaks of the molecular ions of three sterols with M^+ 426, 414, and 412. PMR spectrum (100 MHz, $CDCl_3$, HMDS, δ, ppm): 0.50 (CH_3-18, s), 0.74 (CH_3-19, s), 3.50 (H-3, m), and 5.10 (H-7, m).

Bryonolic Acid (4) — Substance (3), $C_{30}H_{48}O_3$, mp 308-310°C (from C_6H_6) $[\alpha]_D^{22}$ −25.4 ± 2° (*c* 1.1; $CHCl_3$–MeOH, 1:1). IR spectrum (KBr, v, cm^{-1}): 3460 (OH), 1685 (CO of a carboxy group). Mass spectrum, *m/z* (%): M^+ 456 (42.9), 441 (50.0), 438 (14.3), 423 (42.9), 411 (4.3), 410 (7.1), 395 (12.9), 393 (3.6), 381 (4.3), 377 (5.0), 301 (11.4), 287 (12.9), 259 (100), 248 (37.1), 247 (74.3), 241 (78.6), 235 (60.0), 229 (75.7), 221 (37.1), 207 (24.3), 203 (47.1), 189 (67.1.) For the ^1H and ^{13}C NMR spectra, see Tables 1 and 2.

The Mixture of Sterol Glycosides (8), (10), and (12) — Substance (4). GLC [17] showed that the carbohydrate part of the mixture of glycosides (8), (10), and (12) consisted of one molecule of *D*-glucose in each case. PMR spectrum (100 MHz, C_5D_5N, O — HMDS δ, ppm, J, Hz): 0.46 (CH_3-18, s), 0.60 (CH_3-19, s), 4.90 (H-1 *D*-glucopyranose, d, ^3J = 8 Hz), 5.06 (H-7, m).

Isomultiflorenol Acetate (2) from (1). Isomultiflorenol (60 mg) was acetylated with 1 ml of acetic anhydride in 2 ml of pyridine at room temperature for 4 days. The reaction mixture was poured into water and the reaction product that precipitated was filtered off and washed with water. It was then recrystallized from a mixture of chloroform and methanol (1:1), to give 60 mg of the acetate (2), $C_{32}H_{52}O_2$, mp 220-223°C $[\alpha]_D^{22}$ + 29.3 ± 2° (*c* 1.5; $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 1730, 1260 (ester group). Mass spectrum, *m/z* (%): M^+ 468. (46.2), 453 (22.1), 393 (12.5), 301 (40.4), 289 (39.4), 241 (29.8), 229 (40.4), 218 (100), 205 (61.5), 203 (38.5), 191 (17.3), 189 (25). For the PMR spectrum, see Table 1.

Isomultiflorenone (3) from (1). At −4°C, 0.25 ml of the Jones reagent was added to 100 mg of isomultiflorenol (1) in 15 ml of acetone, and the mixture was stirred at the same temperature for 30 min, after which the reaction was stopped by the addition of 1 ml of methanol. The reaction mixture was diluted with water and treated with chloroform. The reaction products were chromatographed on a column, with elution by system 2. Thus gave 75 mg of isomultiflorenone (3) $C_{30}H_{48}O$, mp 180-184°C (from EtOAc), $[\alpha]_D^{22}$ + 80 ± 2° (*c* 0.9; $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 1710 (C=O). CD (*c* 0.077; EtOH): $\Delta\varepsilon$ = +0.84 (290 nm, $\Delta\varepsilon$ = −1.18 (217 nm), $\Delta\varepsilon$ + 1.84 (205 nm). ORD (*c* 0.07; EtOH): $[M]_{305}$ = +2880°, $[M]_{270}$ = +300°. Mass spectrum, *m/z* (%): M^+ 424 (34.2), 409 (23.7), 271 (13.2), 257 (100), 245 (94.7), 218 (18.4), 205 (97.4). For the PMR spectrum, see Table 1.

Bryonolic Acid Acetate (5) from (4). Bryonolic acid (70 mg) was acetylated with 1 ml of acetic anhydride in 2 ml of pyridine at room temperature for 4 days. The reaction mixture was poured into water. The resulting precipitate was filtered off, washed with water, and chromatographed on a column, with elution by chloroform. This gave 30 mg of the acetate (5) $C_{32}H_{50}O_4$, mp. 234-235° (from MeOH), $[\alpha]_D^{20}$ + 20 ± 2° (*c* 0.6; EtOH). IR spectrum (KBr, ν, cm^{-1}): 3470 (OH), 1740; 1255 (ester group), 1705 (C=O of a carboxy group). Mass spectrum, *m/z* (%): 498 (57.1), 483 (57.1), 467 (4.8), 453 (3.2), 438 (8.7), 423 (85.7), 394 (12.7), 301 (100), 289 (57.1), 241 (82.1), 235 (92.9), 229 (82.1), 221 (35.7), 203 (57.1), 189 (85.7). For the PMR spectrum, see Table 1.

Methyl Bryonolate (6) from (4). Bryonolic acid (50 mg) was treated with diazomethane (4 ml) [sic]. After a week, the reaction product was chromatographed on a column, with elution by chloroform. This yielded 32 mg of the methyl ester (6), $C_{31}H_{50}O_3$, mp 137-139° (from EtOH), $[\alpha]_D^{20}$ + 16.7 ± 2° (*c* 0.6; EtOH). IR spectrum (KBr, ν, cm^{-1}): 3550-3450 (OH), 1730, 1240 (ester group). Mass spectrum, *m/z* (%): 470 (67.9), 455 (62.5), 437 (25.0), 411 (19.6), 395 (7.1), 393 (2.7), 377 (4.5), 316 (8.0), 301 (8.9), 262 (28.6), 259 (100), 249 (87.5), 247 (68.8), 241 (62.5), 235 (25.0), 229 (56.3), 207 (25.9), 203 (28.6), 189 (62.5). For the PMR spectrum, see Table 1.

Jones Oxidation of the Mixture of Sterols (7), (9), and (11). In 10 ml of acetone, 112 mg of substance (2) was oxidized with 0.15 ml of the Jones reagent [9] at −5°C for 10 min. The reaction was stopped by the addition of 0.5 ml of methanol. After the usual working up and column chromatography of the products with elution by chloroform, 90 mg of a mixture of the corresponding ketones was obtained. IR spectrum (KBr, ν, cm^{-1}): 1715 (CO at C-3). In the mass spectrum the peaks of molecular ions with M^+ 424, 412, and 410 were clearly traced. PMR spectrum (100 MHz, $CDCl_3$, 0 — HMDS, δ, ppm): 0.50 (CH_3-18, s), 0.94 (CH_3-19), 5.10 (H-7, m).

Smith Degradation of the Mixture of Glycosides (8), (10), and (12). A solution of 200 mg of sodium periodate in 3 ml of water was added to 100 mg of substance (4) in 10 ml of methanol, and the reaction mixture was stirred for 3 h. Then it was poured into water and the excess of oxidant was destroyed with a few drops of ethylene glycol. The products were extracted with chloroform. The chloroform extract was washed with water and evaporated. In small portions, 200 mg of sodium tetrahydroborate was added to the residue in 20 ml of methanol. After the end of the reaction, the mixture was acidified with sulfuric acid and left at room temperature for 1 h. The reaction mixture was diluted with water and treated with chloroform. The chloroform extract was washed with water and evaporated. The residue was recrystallized from chloroform−methanol. The chromatographic behavior of the product in TLC and GLC and its mass spectrum agreed with those of substance (2).

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