

ON THE STRENGTH OF PUNJABI ASPHALT

MICHAL JURÁŠEK^a, JOSEF CABALKA^b, and PAVEL DRAŠAR^a

^a Department of Chemistry of Natural Substances, University of Chemistry and Technology, Technická 5, 166 28 Prague 6-Dejvice, ^b Nové Kounice 37, 364 71 Bochov, Czech Republic michal.jurasek@gmail.com, drjc@mybox.cz, drasarp@vscht.cz

Mumio (shilajit), a substance similar to asphalt or resin that oozes from rocks during hot sunny days, mostly in caves in the Himalayas, is known as a medicinal substance in Eastern medicine. It is slowly being accepted by Western healing as well as medicine. It mainly contains fulvic acids, humic acids and a number of other substances. The article mainly summarizes recent information about this substance.

Keywords: shilajit, mumijo, rasayana, biological activity, properties, fulvic acids

Shilajit (also spelled shilajeet, śilājatu) in Sanskrit शिलाजीत or mumijo (mumio, moomiyo, mumia), Latin Asphaltum punjabianum, is a mostly blackish-brown substance similar to asphalt or resin (Fig. 1), which oozes out of rocks during hot sunny days, mostly in caves in the Himalayas, at altitudes between 1000-5000 m, from Arunachal Pradesh in the east to Kashmir in the west. It is also found in other countries such as Afghanistan, Antarctica, Bhutan, China, Nepal, Pakistan, North East Africa, Tibet and the present day Russian Federation, the most prized being the Kyrgyz Shilajit today. In Eastern medicine, it is thought to slow aging and promote rejuvenation of the body, thus fulfilling Ayurvedic medicine's requirement for classification as a rasayana (रसायन, an early Ayurvedic term related to extending lifespan and strengthening the body). As with the marali root¹, its medicinal properties were pointed out to Asian hunters by game that sought out and licked the shilajit. The origin of mumijo is not entirely clear, but the current view is that they are the organic remains of flora and fauna that have intermixed and com-



Fig. 1. Shilajit, Latin Asphaltum punjabianum

bined with inorganic rock minerals over thousands of years of natural processes².

Shilajit, a substance shrouded in many superstitions, cited e.g. by Avicenna, Aristotle and others (e.g. for coughs, tonsillitis, migraines, epilepsy, fractures, dislocations, poliomyelitis, facial paralysis, poisoning, tuberculosis, ulcers and inflammatory diseases)³, is still very popular and is sold in the form of a dietary supplement by reputable pharmacies. However, like anything that is for sale and of which there is little, shilajit is commonly adulterated and even passed off as almost anything; careful analysis and quality control is in order here⁴. It should be noted that its composition is variable, depending on the place of collection, and hence it has variable biological properties, ranging from zero to "miracle". The ballast "grey" literature and information surrounding this substance is very abundant and not worth quoting. However, the Chemical Abstracts Service lists 298 journal communications, 187 patents, 33 reviews and 6 clinical trial records, mostly from our century, on this material.

If we look at those clinical studies mentioned, it is noted that a 2020 study showed that oral consumption of mummy after tibia fracture surgery could be a promising option for reducing healing time⁵. Results from a 2019 study showed that 8 weeks of mumijo supplementation promoted the maintenance of maximal muscle strength after fatiguing exercise and induced beneficial muscle and connective tissue adaptations⁶. Work from the same year provided evidence showing that oral shilajit supplementation in adult healthy women up-regulated genes relevant to endothelial cell migration and blood vessel growth and improved skin microperfusion⁷. Treatment with shilajit, according to a 2016 study, significantly increased total testosterone, free testosterone, and dehydroepiandrosterone (DHEA) compared to placebo. Gonadotropic hor-

Chem. Listy 117, 547-550 (2023)

mone levels (LH and FSH) remained unchanged⁸. A 2016 study provided evidence that oral shilajit supplementation in overweight/class I obese human subjects promoted skeletal muscle adaptation through upregulation of extracellular matrix-related genes that control muscle mechanotransduction properties, elasticity, repair, and regeneration⁹. A 2009 study demonstrated the spermatogenic effect of shilajit in oligospermic patients as attributed in Ayurvedic medicine¹⁰. It can be further summarized that shilajit has antiulcerogenic, antidiabetic, anxiolytic, immunomodulatory, antiallergic, analgesic, neuroprotective, antifungal, anti-inflammatory and antioxidant properties. Its activity in promoting cognitive and memory functions is also reported¹¹.

Current literature reports the use of shilajit as a nutraceutical in the prevention of Alzheimer disease¹² and cognitive disorders¹³ including those related to old age¹⁴. Shilajit has been and is used alone, and as a component, in Oriental medicine for general physical strengthening, anti-aging, for blood sugar stabilization, for urinary tract rejuvenation, for increased brain functioning, for kidney rejuvenation, for immune system strengthening, for arthritis, hypertension, and also for the treatment of many other diseases¹⁵. Shilajit has been studied as a chemotherapeutic agent for bladder cancer¹⁶. It has been used in the form of an antimicrobial hydrogel to heal wounds¹⁷. However, a case of exercise-induced anaphylaxis following ingestion of shilajit has also been reported¹⁸ as well as a case of pseudohyperaldosteronism following its ingestion during pregnancy¹⁹

The bachelor thesis²⁰ lists a number of other biological activities, including protection from ionizing radiation. However, the thesis is so confusing that some of the information given cannot be found even by citation. The Czech Sisyphus Skeptics Club states that the data on the medicinal properties of shilajit are unreliable² as they are not supported by clinical studies; apparently they can be advised to look into the contemporary medical literature. The above results of clinical trials confirm the validity of including shilajit among rasayans, among others, both for strengthening oligospermic patients and for increasing testosterone and youth hormone concentrations²¹.

Although shilajit is a mixture of a number of substances, it has a Chemical Abstracts Service registration number of 12040-71-0. It can be purchased at the chemical market for approximately 1/g, somewhat more expensive at the pharmacy. Mumijo, when purified of impurities and extracted, takes the form of a dark brown homogeneous mass, elastic in consistency, with a glossy surface, a distinctive aromatic odour and a bitter taste. Specific gravity 2–2.5 kg dm⁻³, melting point ca. 80 °C, pH of a 0.5 % aqueous solution 6.7–7.0 increasing by time to 7.5. During storage, mumijo gradually hardens due to loss of moisture. It is readily soluble in water (1/8), slightly soluble in 95% ethanol (1/4500) and ether (1/7000), almost insoluble in chloroform²².

Let's take a closer look at the composition. The primary constituents of shilajit are biologically active fulvic acids (we use in Czech the progressive nomenclature²³ "fulvová" instead of the term "fulvokyselina") with a molecular weight of 700–2000 Daltons, which make up at least 60 % of shilajit, and oxidized dibenzo- α -pyrones, which make up ca. 0.3% (cit.²⁴). Other components include humins, humic acids, phytophenols, aromatic carboxylic acids (benzoic, hippuric, ellagic), organic acids, amino acids, peptides (mono-, di-, tripeptides), proteins including albumins, lipids, phospholipids fatty acids,

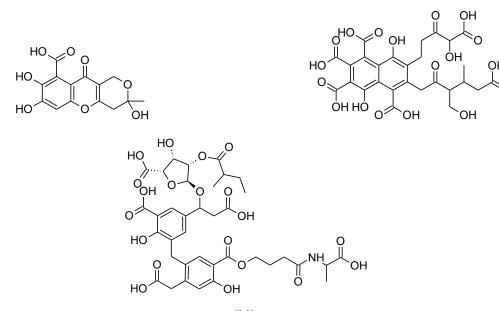


Fig. 2. Different ideas about structure of fulvic acids as cited in^{33–35}



Fig. 3. Dibenzo-α-pyrone (6H-dibenzo[b,d]pyran-6-one)

triterpenes, minerals and water²⁵. Before food and medicinal use, the natural material must be purified, for which a number of procedures are described²⁶. The International Humic Substance Society (IHSS) website²⁷ provides comprehensive analytical data and samples for humic substances that could be used for characterization and identification.

Fulvic acids (from Latin fulvus, yellow, (fulvic substances) CAS RN 308066-67-3) are the yellow-brown fraction of humic substances (complex high molecular weight polycyclic compounds as a not very ordered network of aromatic organic polymers with many carboxylic groups (COOH). These acids readily dissociate and bind metal ions). They have relative molecular weights in the range of several hundred to tens of thousands Da (ref.² probably originating in lignin, and are soluble in both acidic and basic media. Humic acids (sometimes classified as allomelanins²⁹ CAS RN 1415-93-6) can be characterized as a loosely ordered network of aromatic polymers of varying acidity and reactivity³⁰, are black-brown humic substances with molecular weights of five thousand to one hundred thousand, soluble in alkaline solutions but insoluble in acids, even these are capable of binding metal ions. Humins are all other insoluble brown-black humic substances present in soil organic matter which cannot be converted into solution by any acid-base treatment^{23,31,32}

A recent review³⁶ provides a summary showing that fulvic acids can act as an immune modulator, influence redox status and potentially affect gut health. It is described that fulvic acids reduce pro-inflammatory markers, but also activate the immune system to kill bacteria. They have been shown to reduce oxidative stress and even induce apoptosis in liver cancer cell lines. Further, fulvic acids also affect the microbiome and possibly improve gut function. Fulvic acids seem to have a Yin-Yang effect when it comes to these physiological states. However, at high doses and poor administration, their toxicity may also manifest itself.

Again, as with other means of traditional medicine of the Orient^{38,39}, we must be careful not to dismiss the results of medical research that have thousands of years of tradition behind them just because they do not fit into the "boxes" that we, in our traditional understanding, have created in modeling medical and natural phenomena. Yes, one can be cautious about oriental alchemy, for example, although it too has provided some of the foundations for our contemporary chemistry. On the other hand, the experience with natural drugs and their medicinal uses is, perhaps, very useful in researching new drugs, even for such "Western" institutions as National Institutes of Health, Bethesda, MD, whose experts gather advice from rootswomen and shamans all over the globe. And our series of articles, such as^{40,41}, should serve to shed a little light on it.

REFERENCES

- Jurášek M., Opletal L., Harmatha J., Sláma K., Drašar P.: Chem. Listy 115, 595 (2021).
- Heřt J.: Stručný výkladový slovník českých skeptiků. Český klub skeptiků Sisyfos, https://www.sisyfos.cz/ clanek/870-mumio, downloaded June 22, 2022.
- 3. https://www.blackresin.com/shilajit-resins-middleeastern-history/, downloaded June 22, 2022.
- Binitha R. R. V., Mahadevan S., Rosamma M. P., Rajesh K. S.: J. Pharm. Sci. Innovation 8, 189 (2019).
- Sadeghi S. M. H., Hosseini Khameneh S. M., Khodadoost M., Hosseini Kasnavieh S. M., Kamalinejad M., Gachkar L., Rampp T., Pasalar M.: J. Altern. Complementary Med. 26, 521 (2020).
- Keller J. L., Housh T. J., Hill E. C., Smith C. M., Schmidt R. J., Johnson G. O.: J. Int. Soc. Sports Nutr. 16, 1 (2019).
- Das A., El Masry S. M., Gnyawali S. C., Ghatak S., Singh K., Stewart R., Lewis M., Saha A., Gordillo G.,

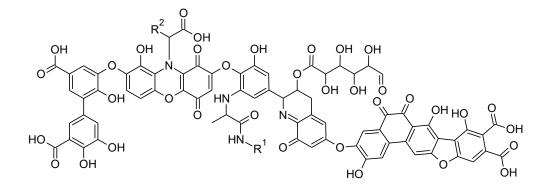


Fig. 4. The idea of humic acid as cited in³⁷, for other ideas see³¹

- Pandit S., Biswas S., Jana U., De R. K., Mukhopadhyay S. C., Biswas T. K.: Andrology 48, 570 (2016).
- 9. Das A., Datta S., Rhea B., Sinha M., Veeraragavan M., Gordillo G., Roy S.: J. Med. Food 19, 701 (2016).
- Biswas T. K., Pandit S., Mondal S., Biswas S. K., Jana U., Ghosh T., Tripathi P. C., Debnath P. K., Auddy R. G., Auddy B.: Andrology 42, 48 (2009).
- 11. Carrasco-Gallardo C., Guzmán L., Maccioni R. B.: Int. J. Alzheimer's Dis. 2012, 674142.
- Calfio C., Gonzalez A., Singh S., Rojo L. E., Maccioni R. B.: J. Alzheimer's Dis. 77, 33 (2020).
- Maccioni R. B., Calfio C., Gonzalez A., Luttges V.: Biomolecules 12, 249 (2022).
- 14. Sharma J.: World J. Pharm. Pharm. Sci. 9, 2054 (2020).
- Malik N., Masand S., Keshav J., Mohapatra S.: World J. Pharm. Res. 9, 455 (2020).
- Kloskowski T., Szeliski K., Krzeszowiak K., Fekner Z., Kazimierski L., Jundzill A., Drewa T., Pokrywczynska M.: Sci. Rep. *11*, 22614 (2021).
- Zandraa O., Ngwabebhoh F. A., Patwa R., Nguyen H. T., Motiei M., Saha N., Saha T., Saha P.: Int. J. Pharm. (Amsterdam, Neth.) 607, 120952 (2021).
- Losa F., Deidda M., Firinu D., Di Martino M. L., Barca M. P., Del Giacco S.: World J. Clin. Cases 7, 623 (2019).
- Stavropoulos K., Sotiriadis A., Patoulias D., Imprialos K., Dampali R., Athyros V., Dinas K.: Gynecol. Endocrinol. 34, 1019 (2018).
- 20. Šmídová H.: Research on applications of humic acids in medicine and cosmetics. Bachelor thesis. Brno University of Technology, Brno 2010; https:// www.vut.cz/www_base/ zav_prace_soubor_verejne.php?file_id=27101, downloaded August 3, 2022.
- 21. Jurášek M., Stárka L., Drašar P.: Chem. Listy 116, 113 (2022).

- 22. https://cs.wikipedia.org/wiki/Mumio, downloaded June 22, 2022.
- 23. Drašar P., Kozler J., Paleta O.: Chem. Letters 117, 581 (2023).
- 24. Ghosal S.: US6440436 (2002).
- 25. Orlov Yu. A., Orlov S. Yu., Sakalova K. L.: RU2164411 (2001).
- 26. Bugaev F., Kompantsev D., Pogrebnyak L.: J. Res. Pharm. 23, 697 (2019).
- 27. https://humic-substances.org/, downloaded June 26, 2022.
- 28. Pivokonský M.: Coagulation in water treatment, Academia, Prague 2020.
- 29. The Merck Index, Monograph Number 4771, Merck, Whitehouse Station 2001.
- 30. Encyclopædia Britannica, Inc.; https:// www.britannica.com/, accessed June 26, 2022.
- Skokanová M., Dercová K.: Chem. Listy 102, 262 (2008).
- 32. Fremrová L.: ISO 6107-5 (75 0175), part 5 (2010).
- http://www.chemspider.com/Chemical-Structure.4514278.html, downloaded June 22, 2022.
- 34. Stevenson F. J.: *Humic Chemistry: Genesis, Composition, Reactions.* Wiley, New York 1994.
- 35. Veselá L., Kubal M., Kozler J., Innemanová P.: Chem. Listy 99, 711 (2005).
- Winkler J., Ghosh S.: J. Diabetes Res. 2018, 5391014 (2018).
- 37. Stevenson F. J.: *Humus Chemistry*. Wiley, New York 1982.
- Jurášek M., Opletal L., Kmoníčková E., Drašar P.: Chem. Listy 115, 363 (2021).
- Bejček J., Spiwok W., Kmoníčková E., Ruml T., Rimpelová S.: Chem. Listy 115, 4 (2021).
- 40. Jurášek M., Drašar P.: Chem. Listy 115, 468 (2021).
- 41. Jurášek M., Rybka A., Opletal L., Drašar P.: Chem. Listy 116, 668 (2022).