Archaeological frankincense

Frankincense, or olibanum, obtained from trees of the genus *Boswellia*[1], is the best known of the aromatic gum resins used throughout the world as incense in religious ceremonies. The earliest archaeological evidence for the burning of incense comes from the Old Kingdom in Ancient Egypt, where spoon-shaped incense burners with long handles have been found. However, no chemical evidence exists of the exact resin used. A wide range of ingredients would have been used by the ancient incense-maker and such materials would have been important traded products[2]. We have chemically characterized frankincense from the archaeological record at the site of the major frontier settlement of Qasr Ibrîm, Egyptian Nubia.

The material (from the Egyptian Exploration Society) came from levels associated with the Post-Meroitic phase of occupation of the site. Samples of amorphous material were recovered during sieving of fill from the cellar of a house dating to around AD 400–500 (Structure X-265)[3].

We characterized the resins by a combination of gas chromatography and mass spectrometry (GC/MS) using solvent solubilization (2:1 v/v, dichloromethane/propan-2-ol), derivatization and pyrolysis techniques[4]. Solvent-soluble fractions showed the presence of pentacyclic triterpenoid components present in modern frankincense resin, as determined by mass spectrometry (Fig. 1). Especially characteristic are the α- and β-boswellic acids (**1** and **2**) and the corresponding *O*-acetyl derivatives (**3** and **4**), which dominate the GC/MS mass chromatograms obtained from both the ancient and modern frankincense (Fig. 2).

These data were supported by detection of 24-noroleana-3,12-diene and 24-norursa-3,12-diene, which are the most abundant components of the Curie-point (610 °C) pyrolysates of the extracted archaeological resin, and reference frankincense. The boswellic acids and their *O*-acetyl derivatives are the major constituents of the fresh aromatic gum resins from *Boswellia* trees[1].

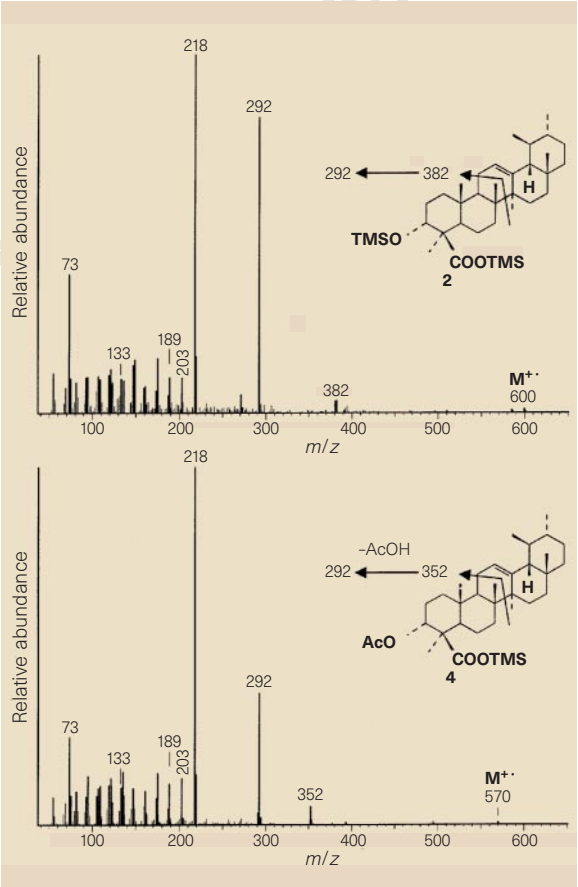
Other pieces of amorphous resin recovered from the same excavations at Qasr Ibrîm comprised tricyclic diterpenoid acids including isopimaric acid, abietic acid and dehydroabietic acid, indicating a pinaceous resin[5]. Although such resins and their derivatives have been reported at archaeological sites[6], we believe that this is the first occasion where diterpenoid and triterpeoid resins have been recovered from the same locality.

Difficulties in detecting frankincense, and similar commodities, in the archaeological record stem from their amorphous nature, which means they are easily overlooked in excavations.

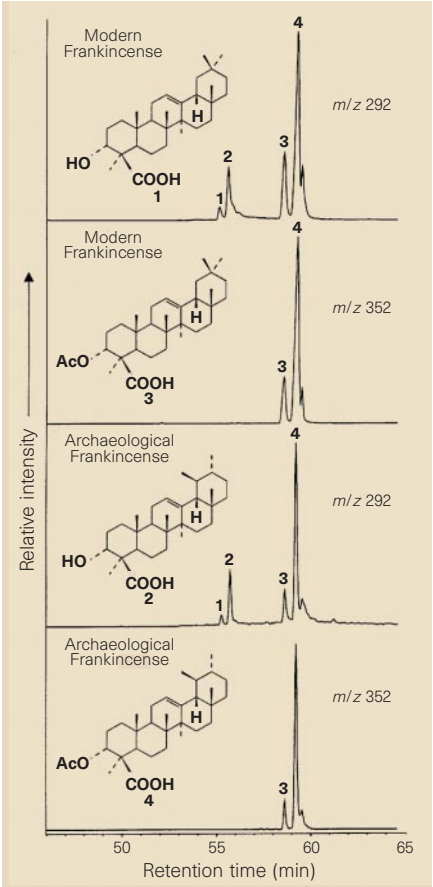
Boswellia did not grow near Qasr Ibrîm, being found mainly in northern Somalia and southern Arabia[7]. The frankincense must therefore have been imported to the middle Nile. The Ancient Egyptians obtained incense from northern East Africa, specifically from the ill-defined area of Punt, but there is no chemical evidence that the material was true frankincense. The earliest documentary evidence for the use of frankincense is in biblical references in the seventh century BC[8,9].

The main period of trade was the Greco-Roman period, when frankincense was shipped by sea from southern Arabia and possibly overland by caravan. Like *Boswellia*, Pinaceae did not grow near Qasr Ibrîm, so the pine resin must also have been imported.

The discovery of similar-sized pieces of the two types of resin in close association may point to their use together in incense-burning ceremonies. By the late Roman period most frankincense seems to have been obtained from the African side of the Red Sea, but the arrival of Christianity in the Mediterranean and Egypt apparently reduced demand for it[10]. This coincides with the date of our finds of frankincense at



◀ **Figure 1** Mass spectrometry of triterpenoids of ancient frankincense. Electron ionization (70 eV) mass spectra of the trimethylsilyl derivatives of β-boswellic acid (upper) and *O*-acetyl-β-boswellic acid (lower) obtained from the GC/MS analysis of ancient frankincense. Insets: structures showing the origins of the fragment ions used to plot characteristic mass chromatograms (Fig. 2).



▶ **Figure 2** Comparison of ancient and modern frankincense. Partial GC/MS mass chromatograms of the trimethylsilylated solvent-soluble fractions of a sample of reference frankincense (from R. White) and of resin recovered from Qasr Ibrîm. The structures shown are: **1,** α-boswellic acid; **2,** β-boswellic acid; **3,** *O*-acetyl-α-boswellic acid; **4,** *O*-acetyl-β-boswellic acid. The *m*/*z* 352 mass chromatograms characterize *O*-acetyl derivatives, the major components of both the ancient and modern resin. The *m*/*z* 292 chromatograms show the similarity of the distributions of the *O*-acetyl and free alcohol forms. Inset: structures of compounds in their natural (underivatized) forms.

Qasr Ibrîm[3,11].
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How pine cones open

The scales of seed-bearing pine cones move in response to changes in relative humidity. The scales gape open when it is dry, releasing the cone's seeds[1]. When it is damp, the scales close up. The cells in a mature cone are dead, so the mechanism is passive: the structure of the scale and the walls of the cells composing the scale respond to changing relative humidity. Dissection of cones from the Monterey pine, *Pinus radiata*, revealed to us two types of scale growing from the main body of the cone — the ovuliferous scale and the bract scale. The larger ovuliferous scales respond to changes in relative humidity when removed from the body of the cone.

The scale consists of two tissues distinguishable with the naked eye (Fig. 1a). The inner surface of the scale is composed of sclerenchyma fibres (8–12 μm in diameter, 150–200 μm long), grouped in bundles reminiscent of cables. The outer surface of the scale is composed of sclerids (20–30 μm diameter, 80–120 μm long).

We mounted a scale on a rigid metal frame and exposed it to controlled and changing relative humidity at 23 °C in an enclosed chamber. Using image analysis, we measured the angle between the scale and the base of the frame, and the distance that the tip of the scale moved. The scale moves towards the centre of the cone in high relative humidity and away from the centre in low relative humidity (Fig. 1b).

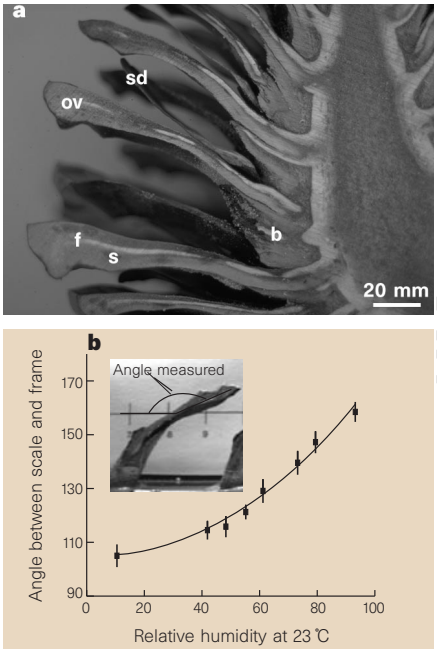

Figure 1 Morphology and behaviour of pine cone scales. **a,** Median longitudinal section of female cone. b, bract scale; sd, seed; ov, ovuliferous scale with two-layer structure consisting of f, fibres (white line within the scale) and s, sclerids. **b,** Graph plotting the angle a scale makes to the base of the experimental apparatus against relative humidity. Inset: experimental apparatus and measured angle. Five scales were used to calculate mean±s.e.m. **c,d,** Scanning electron micrographs of fibres and sclerids, respectively. θ, the angle between the long axis (la) of the cell and the direction of winding of cellulose fibres (cm), is high in sclerids and low in fibres.

We exposed sclerid and fibre cells to a range of relative humidities in a microbalance with a controlled environment and measured the weight changes with time. There were no differences between the two cell types. Chemical analysis[2] showed that each cell type has roughly a 20% volume fraction of cellulose in its cell wall. The rest is lignin, hemicellulose and pectin.

There are large differences in the tensile stiffness (fibre 4.53 ± 0.90 GPa; sclerid 0.86 ± 0.05 GPa). With a 1% change in relative humidity at 23 °C the coefficient of hygroscopic expansion of fibres (0.06 ± 0.02) is significantly lower than that of sclerids (0.20 ± 0.04). Modelling the scale as a simple bilayer structure requires that three parameters are known[3]: the stiffness of the two tissue types, the relative dimensions of each layer and their coefficient of hygroscopic expansion. The movement of the tips of the scales is not significantly different from that predicted by the model[4] (mean, 16.2 mm; predicted, 20.6 mm; $t = 2.25$; 8 d.f.; not significant).

It is not possible to dissect individual cells from the scale as the material is extremely tough. We removed cells using chemical maceration but this removes water and some of the other components of the cell wall. This may affect the observed angle of winding of the microfibrils relative to the long axis of the cell (θ), as may the extremely dry condition under which the cells were observed. Scanning electron micrographs show that θ is considerably lower in fibre cells than in sclerids (Fig. 1c, d). This was confirmed by polarizing light microscopy[5], which indicated that θ is 30° (±2°) for fibre cells and 74° (±5°) for sclerid cells.

The mechanism of bending therefore seems to depend on the way that the orientation of cellulose microfibrils controls the hygroscopic expansion of the cells in the two layers. In sclerids, the microfibrils are wound around the cell (high winding angle) allowing it to elongate when damp. Fibres have the microfibrils orientated along the cell (low winding angle) which resists elongation. The ovuliferous scale therefore functions as a bilayer similar to a bimetallic strip, but responding to humidity instead of heat.

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